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16. ABSTRACT

This report summarizes data on air emissions from the production of vulcanized elastomers (rubbers) and fabrication of rubber products. Hydrocarbons and particulates are emitted from various operations. Hydrocarbon emissions consist of monomers, rubber chemicals, and solvents which are volatilized during processing. Particulate emissions consist primarily of carbon black, soapstone, zinc oxide, and other materials emitted from compounding, grinding, and talc dusting operations. To assess the environmental impact of this industry, source severity was defined as the ratio of the time-averaged maximum ground level concentration of a pollutant emitted from a representative plant to the ambient air quality standard (for criteria pollutants) or to a reduced threshold limit value (for noncriteria pollutants). Source severities were greater than or equal to 1 for the following operations: the butadiene absorption vent in emulsion SBR production, the drying operation in solution SBR production, green tire spraying and curing operations in the tire industry, and rubber cementing in the rubber footwear industry. Emissions from rubber processing are expected to increase 15% over the period 1975 to 1980.

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This report has been reviewed by the Industrial Environmental Research Laboratory-Cincinnati, U.S. Environmental Protection Agency, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the U.S. Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory - Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report contains an assessment of air emissions from the rubber processing industry. This study was conducted to provide a better understanding of the distribution and characteristics of emissions from rubber processing operations. Further information on this subject may be obtained from the Organic Chemicals and Products Branch, Industrial Pollution Control Division.

David G. Stephan
Director
Industrial Environmental Research Laboratory
Cincinnati

PREFACE

The Industrial Environmental Research Laboratory (IERL) of the U.S. Environmental Protection Agency (EPA) has the responsibility for insuring that pollution control technology is available for stationary sources to meet the requirements of the Clean Air Act, the Federal Water Pollution Control Act, and solid waste legislation. If control technology is unavailable, inadequate, or uneconomical, then financial support is provided for the development of the needed control techniques for industrial and extractive process industries. Approaches considered include: process modifications, feedstock modifications, add-on control devices, and complete process substitution. The scale of the control technology programs ranges from bench- to full-scale demonstration plants.

IERL has the responsibility for developing control technology for a large number of operations (more than 500) in the chemical and related industries. As in any technical program, the first step is to identify the unsolved problems. Each of the industries is to be examined in detail to determine if there is sufficient potential environmental risk to justify the development of control technology by IERL.

Monsanto Research Corporation (MRC) has contracted with EPA to investigate the environmental impact of various industries that represent sources of pollutants in accordance with EPA's responsibility, as outlined above. Dr. Robert C. Binning serves as MRC Program Manager in this overall program, entitled "Source Assessment," which includes the investigation of sources in each of four categories: combustion, organic materials, inorganic materials, and open sources. Dr. Dale A. Denny of the Industrial Processes Division at Research Triangle Park serves as EPA Project Officer for this series. Reports prepared in this program are of two types: Source Assessment Documents, and State-of-the-Art Reports.

Source Assessment Documents contain data on pollutants from specific industries. Such data are gathered from the literature, government agencies, and cooperating companies. Sampling and analysis are also performed by the contractor when the available information does not adequately characterize the source pollutants. These documents contain all of the information necessary for IERL to decide whether a need exists to develop additional control technology for specific industries.

State-of-the-Art Reports include data on emissions from specific industries which are also gathered from the literature, government agencies, and cooperating companies. However, no extensive sampling is conducted by the contractor for such industries. Results from such studies are published as State-of-the-Art Reports for potential utility by the government, industry, and others having specific needs and interests.

This study was undertaken to provide information on air emissions from rubber processing. It was initiated by IERL-Research Triangle Park in December 1974; Mr. Kenneth Baker served as EPA Project Leader. The project was transferred to the Industrial Pollution Control Division, IERL-Cincinnati, in October 1975; Mr. Ronald J. Turner of the Organic Chemicals and Products Branch served as EPA Project Leader from that time through completion of the study.

ABSTRACT

This report reviews the state of the art of air emissions from production of vulcanized elastomers (rubbers) and fabrication of rubber products. Nine industries are included: styrene-butadiene rubber (SBR) production; rubber reclaiming; tires and inner tubes; rubber footwear; rubber hose and belting; fabricated rubber products not elsewhere classified; gaskets, packing, and sealing devices; rubber wire-insulating; and tire retreading.

Hydrocarbons and particulates are emitted from various operations in the rubber processing industries. Hydrocarbon emissions consist of monomers, rubber chemicals, and solvents which are volatilized during the processing. Particulate emissions consist of carbon black, soapstone, zinc oxide, etc., which are emitted from compounding, grinding, and talc dusting operations. Particulates are also emitted as mists and solid particles which are formed by condensation of hydrocarbons that are volatilized from rubber material due to the high temperatures involved in curing, molding, and drying operations.

To assess the severity of emissions from rubber processing industries, a representative plant was defined for each industry except SBR production, where separate representative plants were defined for the emulsion polymerization and solution polymerization processes. Source severity was defined as the ratio of the time-averaged maximum ground level concentration of a pollutant emitted from a representative plant to the ambient air quality standard (for criteria pollutants) or to a reduced threshold limit value (for noncriteria pollutants). The following operations have source severities greater than or equal to one: the butadiene absorption vent in emulsion SBR production, the drying operation in solution SBR production, green tire spraying and curing operations in the tire industry and rubber cementing in the rubber footwear industry.

Mass emissions from the nine industries contribute 0.26% and 0.074% respectively to the national totals of hydrocarbons and particulates from all sources. Due to the open nature of most emission points, control of emissions from rubber processing operations includes collection of the contaminated gas and removal of the pollutants from the gas. For control of hydrocarbon emissions, carbon adsorption with solvent recovery and incineration with heat recovery have been used. Particulate control devices used in the industry include wet scrubbers, cyclones, and baghouses.

This report was submitted in partial fulfillment of Contract No. 68-02-1874 by Monsanto Research Corporation under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period December 1974 to July 1977, and work was completed as of July 1977.

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ABBREVIATIONS AND SYMBOLS

A -- affected area
AAQS -- ambient air quality standard
C -- generally achieved control efficiency
c -- amount of volatile materials lost during vulcanization
c_o -- initial weight percent of component
$\overline{D}$ -- composite population density
D_i -- population density for state i
e -- 2.72
EPR -- ethylene propylene rubber
E_r -- representative emission factor
E_u -- uncontrolled emission factor
F -- hazard factor, equal to the primary ambient air quality standard for criteria pollutants or to a reduced TLV for other pollutants
H -- effective emission height
m -- a constant
Q -- mass emission rate
R -- thickness of rubber stock
S -- source severity
SBR -- styrene-butadiene rubber
t -- averaging time
t' -- time
TLV -- threshold limit value
t_o -- short-term averaging time, 3 min
U -- utilization factor
$\overline{u}$ -- average wind speed
x -- downwind distance from source
σ_z -- vertical dispersion coefficient
$\overline{\chi}(x)$ -- annual mean ground level concentration
χ_{max} -- instantaneous maximum ground level concentration
$\overline{\chi}_{max}$ -- time-averaged maximum ground level concentration

CONVERSION FACTORS AND METRIC PREFIXES[a]

CONVERSION FACTORS

To convert from	to	Multiply by
Degree Celsius (°C)	Degree Fahrenheit	$t_F^\circ = 1.8\ t_C^\circ + 32$
Gram/kilogram (g/kg)	Pound/ton	2.000
Kilogram (kg)	Pound-mass (avoirdupois)	2.204
Kilogram (kg)	Ton (short, 2,000 pound mass)	1.102×10^{-3}
Meter (m)	Angstrom	1.000×10^{10}
Meter (m)	Foot	3.281
Meter (m)	Micron	1.000×10^{6}
Meter (m)	Mile	6.215×10^{-4}
Meter^2 (m^2)	Foot^2	1.076×10^{1}
Meter^3 (m^3)	Barrels (42 gallon)	6.293
Meter^3 (m^3)	Foot^3	3.531×10^{1}
Meter^3 (m^3)	Gallon (U.S. liquid)	2.642×10^{2}
Metric ton	Kilogram	1.000×10^{3}
Metric ton	Ton (short, 2,000 pound mass)	1.102
Pascal (Pa)	Pound-force/inch^2 (psi)	1.450×10^{-4}
Radian (rad)	Degrees (°)	5.730×10^{1}

METRIC PREFIXES

Prefix	Symbol	Multiplication factor	Example
Kilo	k	10^3	5 kg = 5×10^3 grams
Mega	M	10^6	5 Mm = 5×10^6 meters
Milli	m	10^{-3}	5 mm = 5×10^{-3} meter
Micro	µ	10^{-6}	5 µm = 5×10^{-6} meter
Nano	n	10^{-9}	5 nm = 5×10^{-9} meter

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[a] Standard for Metric Practice. ANSI/ASTM Designation: E 380-76$^\varepsilon$, IEEE Std 268-1976, American Society for Testing and Materials, Philadelphia, Pennsylvania, February 1976. 37 pp.

SECTION 1

INTRODUCTION

The rubber processing source type considered in this report includes the major industries involved in either production of synthetic and reclaimed rubber or fabrication of rubber products from natural, synthetic, and reclaimed rubber. The operation of these rubber processing plants constitutes a source of air pollution. The objective of this work was to review the state of the art of air emissions from rubber processing industries and to assess the environmental impact of these emissions. Emission data used in preparation of this report were obtained from literature and government sources.

The major results of this study are summarized in Section 2. The detailed description of the source type in Section 3 includes a general industry description, the manufacturing plant geographical distribution, and an outline of the processes involved. Atmospheric emissions from rubber processing plants are discussed in Section 4. In this section, the emission points, species of emissions, and emission factors from each rubber processing industry are identified and quantified, and environmental effects resulting from these emissions are presented. Present and future aspects of pollution control technology in the rubber processing industries are considered in Section 5. The projected industry growth and anticipated technological developments are discussed in Section 6.

SECTION 2

SUMMARY

Rubber processing is defined in this assessment as either production of vulcanizable elastomers (rubbers) or fabrication of rubber products from natural, synthetic, and reclaimed rubber. The industries included can be categorized into nine Standard Industrial Classification (SIC) codes: 1) SIC 2822--styrene-butadiene rubber (SBR) production; 2) SIC 3031--rubber reclaiming; 3) SIC 3011--tires and inner tubes; 4) SIC 3021--rubber footwear, 5) SIC 3041--rubber hose and belting; 6) 3069--fabricated rubber products N.E.C.;[a] 7) SIC 3293--gaskets, packing, and sealing devices; 8) SIC 3357--wire insulating; and 9) SIC 7534--tire retreading. The 1975 production rates of the above nine industries are shown in Table 1.

TABLE 1. PRODUCTION RATE, EMISSION FACTORS, AND MASS EMISSIONS FOR RUBBER PROCESSING INDUSTRIES

Industry	1975 production, 10^3 metric ton	Emission factors, g/kg product		Mass emissions for 1975, metric tons/yr		Percent contribution to national total emissions	
		Hydrocarbons	Particulates	Hydrocarbons	Particulates	Hydrocarbons	Particulates
SBR production (SIC 2822)	1,179	5.1[a]	0.35[a]	6,000[b]	4.0	0.024	0.0023
Rubber reclaiming (SIC 3031)	83	3.0	1.1	250	91	0.0010	0.0005
Tires and inner tubes (SIC 3011)	2,038[c,d]	16.1	3.6	33,000	7,300	0.13	0.041
Rubber footwear (SIC 3021)	140	99.3	2.9	14,000	400	0.056	0.0022
Hose and belting (SIC 3041)	400	6.6	1.1	2,600	440	0.010	0.0025
Fabricated products N.E.C. (SIC 3069)	997[e]	6.2[e]	3.1[e]	6,200	3,100	0.025	0.017
Gaskets, packing, and sealing devices (SIC 3293)	160	8.3	3.1	1,300	500	0.0052	0.0028
Wire insulating (SIC 3357)	51[e]	3.5[e]	1.1[e]	180	56	0.0007	0.0003
Tire retreading (SIC 7534)	475[c]	4.2	2.0	2,000	950	0.0080	0.0053
TOTAL	N.A.[f]	N.A.	N.A.	65,000	13,200	0.26	0.074

[a] Represents the composite emission factor for emulsion and solution polymerization.

[b] 63% of this is emitted from emission polymerization; the remaining 37% is from solution polymerization.

[c] Average weight of a tire is 10.9 kg.

[d] Inner tubes and other tire materials, which constitute 3% of the industry economy.

[e] Based on amount of rubber compound consumed.

[f] Not applicable.

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[a] Not elsewhere classified.

There are approximately 1,700 rubber processing plants in 43 states.[a] About 25% of these plants are located in Ohio and California. Another 25% are located in Illinois, New York, New Jersey, and Massachusetts. The remaining 50% of the plants are distributed among the other 37 states.

SBR is produced by either emulsion or solution polymerization, with the former process constituting 90% of present production and the latter representing the remaining 10%. Operations in rubber reclaiming include size reduction, fiber separation, depolymerization, drying, and finishing. Fabrication of rubber products involves a number of steps such as compounding, milling, calendering, extrusion, fabric cementing, rubber cementing, molding, and curing.

Hydrocarbons and particulates are emitted from various operations in the rubber processing industries. Hydrocarbon emissions consist of monomers, rubber chemicals, and solvents which are volatilized during the processing. Particulates consist of carbon black, soapstone, zinc oxide, etc., which are emitted during compounding, grinding, and talc dusting operations. Particulates are also emitted as mists and solid particles which are formed by condensation of hydrocarbons that are volatilized from rubber material due to temperatures involved in the processing.

Emission factors and mass emissions from rubber processing industries are summarized in Table 1. Mass emissions from the nine industries constitute 0.26% and 0.074%, respectively, of the national totals of hydrocarbons and particulates emitted from all sources. On the individual state basis, New Hampshire is the only state which has emissions of at least one criteria pollutant[b] from rubber processing that exceeds 1% of the state total emissions of that pollutant.

To quantify the hazard potential of emissions from each emission source, a source severity, S, was defined as:

$$S = \frac{\overline{X}_{max}}{F}$$

where $\overline{X}_{max}$ is the time-averaged maximum ground level concentration of each pollutant emitted from a representative rubber processing plant. F is the primary ambient air quality standard for criteria pollutants and is the "reduced" threshold limit value (TLV® • 8/24 • 1/100) for other pollutants.

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[a] This represents the total number of plants in each of the nine industries except for SIC 7534, where only the plants that could be identified were included.

[b] Criteria pollutants in this study are hydrocarbons, particulates, carbon monoxide (CO), sulfur oxides (SO_x), and nitrogen oxides (NO_x), all of which have national ambient air quality standards established.

One representative plant was defined for each type of rubber processing, except for SBR production. For the latter, two representative plants were defined, one for emulsion polymerization, the other for solution polymerization. Factors considered in defining these representative plants are summarized in Table 2.

TABLE 2. PARAMETERS USED FOR REPRESENTATIVE PLANTS

Population density around the plant: 103 persons/km^2
Wind velocity around the plant: 4.5 m/s

Industry	Annual production, metric tons/yr	Emission height, m
SBR by emulsion (SIC 2822)	41,000	20
SBR by solution (SIC 2822)	41,000	20
Rubber reclaiming (SIC 3031)	14,000	20
Tires and inner tubes (SIC 3011)	20,000	15
Rubber footwear (SIC 3021)	2,700	15
Hose and belting (SIC 3041)	6,500	15
Fabricated products N.E.C. (SIC 3069)	1,700	15
Gaskets, packing, and sealing devices (SIC 3293)	1,700	15
Wire insulating (SIC 3357)	3,000	15
Tire retreading (SIC 7534)	450	15

Using Gaussian plume dispersion theory together with the emission factors and parameters for representative plants, source severities were calculated for each emission source in each of the nine industries. These source severities are summarized in Tables 3 and 4 for elastomer plants and rubber products plants, respectively.

TABLE 3. SOURCE SEVERITIES FOR REPRESENTATIVE ELASTOMER PLANTS[a]

Emission source	SBR emulsion polymerization (SIC 2822)				SBR solution polymerization (SIC 2822)					Rubber reclaiming (SIC 3031)	
	Criteria pollutants		Chemical substances		Criteria pollutants		Chemical substances			Criteria pollutants	
	Hydrocarbons	Particulates	Styrene	Butadiene	Hydrocarbons	Particulates	Styrene	Butadiene	Hexane	Hydrocarbons	Particulates
Styrene storage (breathing)	0.01		0.001		0.01		0.001				
Hexane storage (breathing)					0.03				0.002		
Storage area (fugitive)	0.02		0.002		0.02		-[b]	-[b]	-[b]		
Reactor area (fugitive)	0.2		-[b]	-[b]	0.2		-[b]	-[b]	-[b]		
Butadiene absorption	1		-[b]	0.001							
Monomer recovery area (fugitive)	0.05		-[b]	-[b]							
Desolvent area (surge vent)					0.7		-[b]	-[b]	-[b]		
Desolvent area (fugitive)					0.1		-[b]	-[b]	-[b]		
Purification area (fugitive)					0.1		-[b]	-[b]	-[b]		
Carbon black operation		0.07				0.07					
Size reduction											0.08
Depolymerization										0.5	
Drying	0.3	0.005	0.02	-[b]	9	0.005			0.8		
Baling		0.007				0.007					0.008

[a] Blanks indicate no emissions from unit operations. [b] Not calculated due to lack of data.

TABLE 4. SOURCE SEVERITIES FOR REPRESENTATIVE RUBBER PRODUCT PLANTS[a]

Emission source	SIC 3011		SIC 3021		SIC 3041		SIC 3069		SIC 3293		SIC 3357		SIC 7534	
	Hydrocarbons	Particulates	Hydrocarbons	Particulates	Hydrocarbons	Particulates	Hydrocarbons	Particulates	Hydrocarbons	Particulates	Hydrocarbons	Particulates	Hydrocarbons	Particulates
Compounding	0.1	0.2	0.02	0.03	0.04	0.07	0.01	0.02	0.01	0.02	0.02	0.03		
Milling	0.09		0.01		0.03		0.006		0.008		0.01			
Calendering	0.09		0.01		0.03		0.006		0.008					
Fabric cementing	0.4				0.3									
Extrusion	0.09				0.003		0.001				0.002			
Undertrade cementing	0.4													
Green tire spraying	4													
Buffing														0.01
Rubber cementing			6		0.1								0.03	
Latex dipping and drying			0.01				0.005							
Bonding of extruded parts							0.008							
Adhesive spraying							0.07		0.1					
Molding			0.1	0.03			0.06	0.03	0.2	0.03				
Curing	2	0.5	0.1	0.02	0.4		0.07				0.2		0.008	
Finish painting													0.004	

[a] Blanks indicate no emissions from unit operations.

The number of persons exposed to an annual average ground level concentration ($\overline{\chi}$) of a pollutant from a representative plant for which $\overline{\chi}/F$ is greater than 0.1 and $\overline{\chi}/F$ is greater than 1 was estimated and designated as "affected population." The calculation was made for each pollutant and for each operation with a source severity greater than 0.1. The largest number of persons affected by any operation in each industry is given in Table 5 for both $\overline{\chi}/F$ is greater than 0.1 and $\overline{\chi}/F$ is greater than 1.

TABLE 5. AFFECTED POPULATION BY INDUSTRY

Industry code	Number of persons where $\overline{\chi}/F>0.1$	Number of persons where $\overline{\chi}/F>1$
SIC 2822 (emulsion)	500	20
SIC 2822 (solution)	4,000	300
SIC 3031	200	0
SIC 3011	800	60
SIC 3021	1,000	100
SIC 3041	80	0
SIC 3069	0	0
SIC 3293	20	0
SIC 3357	20	0
SIC 7534	0	0

The consumption of rubber in rubber products fabrication is expected to increase at an average (simple) annual rate of 3% between 1975 and 1980. Assuming that the same level of control exists in 1980 as in 1975, emissions from rubber processing will increase by 15% over that period.

Because most of the rubber processing operations resulting in air emissions are not enclosed, the control of emissions from these sources involves collection of the contaminated gas and removal of the pollutants from the gas. Most rubber processing plants have some types of particulate control devices. Only a few operations have hydrocarbon control equipment installed. Control devices used in the industry for particulate control include wet scrubbers, cyclones, and baghouses. For hydrocarbons, carbon adsorption with solvent recovery and incineration with heat recovery have been used. Overall control efficiency for particulates ranges from 70% to 90%. For hydrocarbons it ranges from 40% to 90%, largely dependent on the gas collection efficiency.

SECTION 3

SOURCE DESCRIPTION

SOURCE DEFINITION

This source type includes the major industries involved in either production of synthetic and reclaimed rubber (vulcanizable elastomers) or fabrication of rubber products from natural, synthetic, and reclaimed rubber. Natural rubber production is not included because no natural rubber is produced in the United States. The industries in this source type can be categorized into nine Standard Industrial Classification (SIC) codes, defined by the U.S. Government as follows (1):

- Synthetic Rubber (Vulcanizable Elastomers) (SIC 2822)
  This industry "comprises establishments primarily engaged in the manufacture of synthetic rubber by polymerization or copolymerization. An elastomer, for the purpose of this classification, is a rubberlike material capable of vulcanization, such as copolymers of butadiene and styrene or butadiene and acrylonitrile, polybutadienes, chloroprene rubbers, and isobutylene-isoprene copolymers." (Only the production of styrene-butadiene rubber is considered in this assessment.

- Tires and Inner Tubes (SIC 3011)
  This industry "includes establishments primarily engaged in manufacturing pneumatic casings, inner tubes, and solid and cushion tires for all types of vehicles, airplanes, farm equipment, and children's vehicles; tiring; and camelback and tire repair and retreading materials."

- Rubber and Plastics Footwear (SIC 3021)
  This industry "includes establishments primarily engaged in manufacturing all rubber and plastics footwear. . . having rubber or plastic soles vulcanized to the uppers." (Processes specific to the utilization of plastics within this industry are excluded from further consideration in the assessment of the rubber processing source.)

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(1) Standard Industrial Classification Manual, 1972. Executive Office of the President, Office of Management and Budget, Washington, D.C., 1972. 649 pp.

- Reclaimed Rubber (SIC 3031)
  This industry "includes establishments primarily engaged in reclaiming rubber from scrap rubber tires, tubes, and miscellaneous waste rubber articles by processes which result in devulcanized, depolymerized, or regenerated replasticized products containing added ingredients. These products are sold for use as a raw material in the manufacture of rubber goods with or without admixture with crude rubber or synthetic rubber."

- Rubber and Plastics Hose and Belting (SIC 3041)
  This industry "includes establishments primarily engaged in manufacturing rubber and plastics hose and belting, including garden hose." (Processes specific to the utilization of plastics within this industry are excluded from further consideration in the assessment of the rubber processing source.)

- Fabricated Rubber Products N.E.C. (SIC 3069)
  This industry "includes establishments primarily engaged in manufacturing industrial and mechanical rubber goods, rubberized fabrics and vulcanized rubber clothing, and miscellaneous rubber specialties and sundries."

- Gaskets, Packing, and Sealing Devices (SIC 3293)
  This industry "includes establishments primarily engaged in manufacturing gaskets, gasketing materials, compression packing, molded packings, oil seals, and mechanical seals. Included are gaskets, packing, and sealing devices made of leather, rubber, metal, asbestos, and plastics." (Only the segment of this industry which utilizes rubber is considered in the assessment of the rubber processing source.)

- Nonferrous Wiredrawing and Insulating (SIC 3357)
  This industry "includes establishments primarily engaged in drawing and insulating, and insulating wire and cable of nonferrous metals from purchased wire bars, rods, or wire." (Only the segment of this industry which utilizes rubber is considered in this assessment.)

- Tire Retreading and Repair Shops (SIC 7534)
  This industry "includes establishments primarily engaged in repairing and retreading automotive tires. Establishments classified here may either retread customers' tires or retread tires for sale or exchange to the user or the trade."

The nine industries defined above can be separated into two industry categories: the elastomer industries and the rubber products industries. The former produce rubber materials; the latter are concerned with consumption of rubber. This classification is illustrated as follows:

Elastomer industries	Rubber products industries
Synthetic rubber (SIC 2822)	Tire and inner tubes (SIC 3011)
Reclaimed rubber (SIC 3031)	Rubber footwear (SIC 3021)
	Rubber hose and belting (SIC 3041)
	Fabricated rubber products N.E.C. (SIC 3069)
	Rubber gaskets, packing, and sealing devices (SIC 3293)
	Rubber wire-insulating (SIC 3357)
	Tire retreading and repairing (SIC 7534)

Following is a general description of these two industry categories:

Elastomers Industry

Synthetic Rubber (SIC 2822)--

The synthetic rubber (elastomer) industry produces high polymers with special, unique properties. Elastomers are considered apart from other polymeric materials because of these unusual properties and because they generally do not lend themselves to plastics uses. By definition, the synthetic elastomer activities start with a monomer, other active chemicals, or with natural elastomeric polymers, and terminate with the formation of a marketable, rubberlike material.

The major raw materials are active monomer, certain chemicals with active end groups, or natural elastomers which are compounded or modified. Many of the same monomers are used in the synthetic elastomer industry as are used in plastics and fibers. Table 6 shows the 1975 production of synthetic elastomers (2). Natural elastomers were not included because they are not produced in the United States. For the past few years (1970 to 1975), approximately 78% of the new elastomers consumed in the U.S. were synthetic; consumption of natural elastomers amounted to 22% (3).

The chemical composition of an elastomer depends solely on the monomers, active chemicals, or natural materials used. The raw materials, or feedstocks, also determine the type and properties of the product produced. The properties of the products are, in turn, usually determined by their end use. The structure, molecular weight, and various properties of elastomers are also determined by the polymerization process, as well as by the catalysts, shortstops, antioxidants, and other ingredients used.

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[a] Only the production of *styrene-butadiene rubber* is covered in this assessment.

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(2) Facts and Figures for Chemical Industry. Chemical and Engineering News, 55(23):39-79, 1977.

(3) Year of Recovery for Rubber Suppliers. Rubber World, 175(4):35-37, 1977.

TABLE 6. 1975 U.S. PRODUCTION OF SYNTHETIC ELASTOMERS

Product type	1975 Production, 10^3 metric tons
Styrene-butadiene rubber[a]	1,179
Butyl rubber	80
Neoprene	144
Nitrile rubber	55
Polybutadiene	290
Polyisoprene	61
Ethylene-propylene	84
Others[b]	47
TOTAL	1,940

[a] Excludes high styrene latex.

[b] Includes polyacrylate, polyalkylene sulfide, chlorosulfonated polyethylene, polyisobutylene, fluorocarbon silicone, and polyurethane elastomers. Polyurethane foam is excluded because it is a plastic material which is considered in SIC 2821.

As shown in Table 6, among the various synthetic rubbers, styrene-butadiene has by far the largest production figure, representing 61% of total synthetic rubber production. It is this segment of the synthetic rubber industry that is considered in the present study.

Reclaimed Rubber (SIC 3031)--
Reclaimed rubber is the product resulting from the treatment of ground scrap tires, tubes, and miscellaneous waste rubber articles with heat and chemical agents to facilitate devulcanization or regeneration of the rubber compound to its original plastic state. It can be used as a partial or complete replacement for new rubber in many fabricated rubber products.

It has been reported (4) that the 1975 production of reclaimed rubber in the United States amounted to 83,000 metric tons.[a]

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[a] 1 metric ton equals 10^6 grams; conversion factors and metric system prefixes are presented in the prefatory material.

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(4) Hoogheem, T. J., C. T. Chi, G. M. Rinaldi, R. J. McCormick, and T. W. Hughes. Identification and Control of Hydrocarbon Emissions from Rubber Processing Operations. Contract 68-02-1411, Task 17, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina. (Final report submitted to the EPA by Monsanto Research Corporation, July 1977.) 383 pp.

Rubber Products Industry

Consumption of new and reclaimed rubber by the industry can be reported in three parts: 1) tires and tire products, including pneumatic and solid tires, inner tubes, and tire retread and repair materials; 2) other products, including footwear, belts, hose, mechanical goods, foam sponge, and sundries; and 3) wire and cable. This breakdown permits observation of trends in total new rubber consumption. It also illustrates the dominant position of tires and tire products, which consistently use 62% to 66% of all new rubber each year (5). Wire and cable use a small part of the total, which has remained constant in absolute terms but has declined from 3% to 1% over the years from 1958 to 1972 (5). The other products consume the remainder (about one-third) of total new rubber production in manufacturing a great variety of items (5).

The reported production figures for the rubber products industry in the seven SIC codes are presented in Table 7 for 1975 (4).

TABLE 7. PRODUCTION OF RUBBER PRODUCTS IN 1975 (4)

SIC code	Industry	1975 Production, 10^3 metric tons[a]
3011	Tires and inner tubes	2,038[b,c]
3021	Rubber footwear	140
3041	Rubber hose and belting	400
3069	Fabricated rubber products N.E.C.	997[d]
3293	Gaskets, packing, and sealing devices	160
3357	Nonferrous wire drawing and insulating	51[d]
7534	Tire retreading and repair	475[b]

[a] Based on product weight except otherwise noted.

[b] Average weight of a tire is 10.9 kg.

[c] Inner tubes and other tire materials, which constitute 7% of the industry economy, are not included here.

[d] Based on amount of rubber compound consumed.

PROCESS DESCRIPTION

Elastomer Production

Styrene-Butadiene Rubber--

Styrene-butadiene rubber (SBR) is a copolymer of styrene (or vinyl benzene, $CH_2{=}CH{-}C_6H_5$) and butadiene ($CH_2{=}CH{-}CH{=}CH_2$). With the exception of some special grades, the styrene content is 23.5 wt %; i.e., a molecular proportion in the chains of one styrene unit to about six butadiene units (6). It is produced by two different processes. The first, emulsion polymerization, accounts for 90% of the total SBR production. Solution polymerization, the newer of the two, accounts for the other 10% of production (7). Butadiene and styrene monomers are the chief raw materials required to manufacture SBR. Others required in smaller amounts are the various emulsifiers, modifiers (e.g., thiols), catalysts, shortstops, coagulating agents, antioxidants, and antiozonants (8).

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(5) Richardson, J., and M. Herbert. Forecasting in the Rubber Industry. Presented at the Joint Meeting of the Chemical Marketing Research Association and the Commercial Development Association, New York, New York, May 1974.

Emulsion Polymerization--Emulsion polymerization is basically the polymerization of monomer droplets suspended in dilute aqueous solution and stabilized by an emulsifier. In this process, the polymerization reaction is initiated by free radicals generated in the water phase. After the emulsifier forms spherical aggregates or molecules called "micelles," monomer swells the micelles, free radicals initiate polymerization, and a new phase is formed; namely, latex particles. Monomer droplets in the aqueous phase decrease in number and completely disappear at about 60% conversion (4). Monomer in the latex particles can be reacted to completion, but the polymerization rate decreases gradually with conversion.

SBR is produced by emulsion polymerization as either rubber latex or rubber crumb. The processes for each of these two types of rubber are discussed below (4, 6-8).

Crumb rubber--A schematic flow diagram for crumb rubber production by emulsion polymerization is presented in Figure 1. Some monomers have inhibitors added to prevent premature polymerization during shipment and storage. The inhibitor is removed before polymerization by passing the monomer through a caustic scrubber in which a 20% NaOH solution is circulated.

Soap solution, catalyst, activator, and modifier are added to the mixture of monomers before polymerization. The soap solution is used to emulsify the monomers in an aqueous medium. The ingredients of this solution are generally a rosin acid soap and a fatty acid soap. The catalyst, usually a hydroperoxide or a peroxysulfate, is a free-radical initiator. The activator facilitates the generation of free radicals more rapidly and at lower temperatures than thermal decomposition alone. The modifier adjusts the chain length and molecular weight distribution of the polymeric rubber during its formation.

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(6) Allen, P. W. Natural Rubber and the Synthetics. John Wiley & Sons, Inc., New York, New York, 1972. 255 pp.

(7) Development Document for Effluent Limitation Guidelines and New Source Performance Standards for the Tire and Synthetic Segment of the Rubber Processing Point Source Category. EPA-440/1-74/013-a, U.S. Environmental Protection Agency, Washington, D.C., February 1974. pp. 31-35.

(8) Morton, M. Rubber Technology, Second Edition. Van Nostrand Reinhold Company, New York, New York, 1973. 603 pp.

Polymerization proceeds stepwise in a series of reactors. The reactor train can produce either "cold" (4°C to 7°C, 0 kPa to 200 kPa) or "hot" (50°C, 380 kPa to 520 kPa) SBR. For "cold" polymerization, the monomer/additives emulsion is cooled prior to reaction, generally using an ammonia or methanol refrigerant cooling medium. Each reactor has its own set of cooling coils (to remove the heat of reaction) and each is agitated by a mixer. The residence time in each vessel is approximately 1 hr. Conversion of monomer to rubber is ordinarily carried out to 60% or less. The reaction mixture is a milky white emulsion called latex.

Shortstop solution is added to the latex exiting the reactors to terminate polymerization at the desired conversion. Two common shortstops are sodium dimethyl dithiocarbamate [$(CH_3)_2NCSSNa$] and hydroquinone (1,4-dihydroxybenzene). The "stopped" latex is held in blowdown tanks which serve as flow-regulating holding tanks.

Economics of synthetic rubber production require recovery and purification of unreacted monomers which may comprise 10% to 40% of the rubber latex solution. Butadiene is first stripped from the latex in a vacuum flash tank at about 20°C to 30°C. The butadiene vapors are absorbed or adsorbed and condensed, and recycled to the feed area for mixing with fresh monomer. Styrene is recovered from the latex in perforated plate-stripping columns which operate with steam injection at 60°C. The steam-styrene vapor mixture is condensed, followed by decanting the styrene and water. The top styrene layer is recycled.

An antioxidant is added to the stripped latex in a blend tank to protect the polymer from oxidation. Different batches, recipes, or dilutions of the stabilized latex can now be mixed in the blend tanks.

The latex is transferred from the blend tank to the coagulator where dilute sulfuric acid (pH 4.0 to 4.5) and sodium chloride solution are added. This acid-brine mixture, called the "coagulation liquor," causes the rubber to precipitate out of the latex. Carbon black and/or extender oils can be added to the rubber latex during coagulation; carbon black is added as an aqueous slurry (approximately 5 wt %), and the oil in an aqueous emulsion.

The precipitated crumb is separated from the coagulation liquor on a shaker screen. The screened crumb is washed with water in a reslurry tank to remove extraneous compounds, particularly

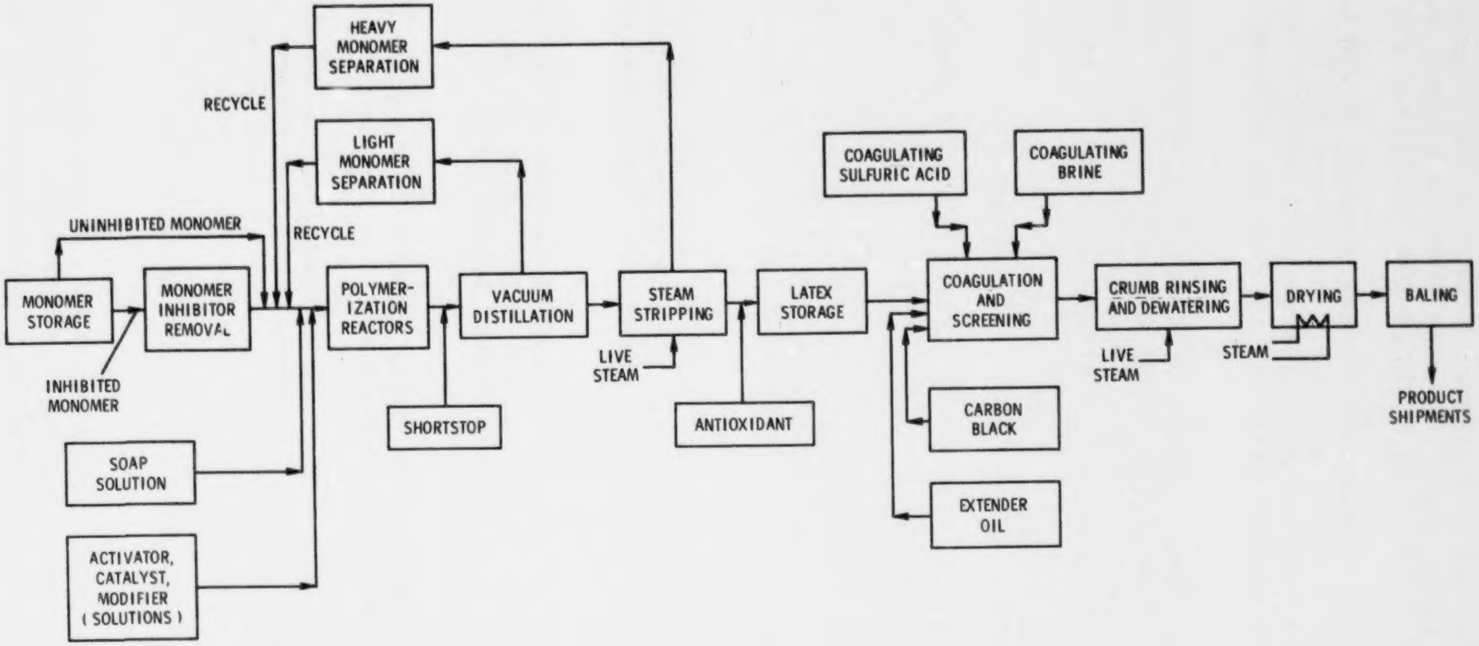

Figure 1. Schematic flow diagram for crumb rubber production by emulsion polymerization (8).

residual coagulation liquor. The crumb rubber slurry is next dewatered using vacuum filtration. Coagulation liquor blowdown and crumb slurry water overflows are usually passed through separators called crumb pits to trap the floatable crumb rubber.

The rinsed, filtered rubber solids are finally dried with hot air (50°C to 120°C) in a continuous belt or screen dryer. After drying, the rubber is weighed and pressed into bales. Normally, bales of synthetic rubber weigh 34 kg and are wrapped in polyethylene film.

Latex rubber--Latex rubber production includes the same processing steps as emulsion crumb production with the exception of latex coagulation and crumb rinsing, drying, and baling. In some instances, the latex polymerization reaction is taken to completion (98% to 99% conversion) as opposed to 60% conversion for emulsion crumb rubber. Therefore, in these instances, the recovery of unreacted monomers is not economical.

Monomer inhibitors are removed by scrubbing with caustic soda. Soap solution, catalysts, and modifiers are added to the monomer(s) prior to feeding the reactors. Fewer reactors are generally used than for emulsion crumb production. Most latexes are made by the "cold" process with the polymerization temperature kept at about 4°C to 7°C. After polymerization, the latex is sent to a blowdown tank for holding. At this point, stabilizers are added.

Latex passes from the storage tanks to a vacuum stripper for removal of unreacted butadiene. Excess styrene is separated from the latex in a steam stripper, condensed, containerized, and sent to disposal.

The stripped latex is passed through a series of screen filters to remove undesirable large solids. The latex is then stored in blending tanks for mixing with other ingredients of the final product such as antioxidants.

A schematic flow diagram for latex rubber production by emulsion polymerization is shown in Figure 2.

Solution Polymerization--Solution polymerization is the newer process for the production of synthetic crumb rubber in the United States. Solution polymerization systems permit the use of stereospecific Ziegler-Natta or alkyllithium catalysts, which allow polymerization of monomers, in an appropriate organic solvent to obtain the *cis* structure characteristic of the natural rubber molecule.

In contrast to emulsion polymerization, where approximately 60% conversion of monomer to polymer is achieved, solution polymerization systems typically proceed to conversion levels in excess of

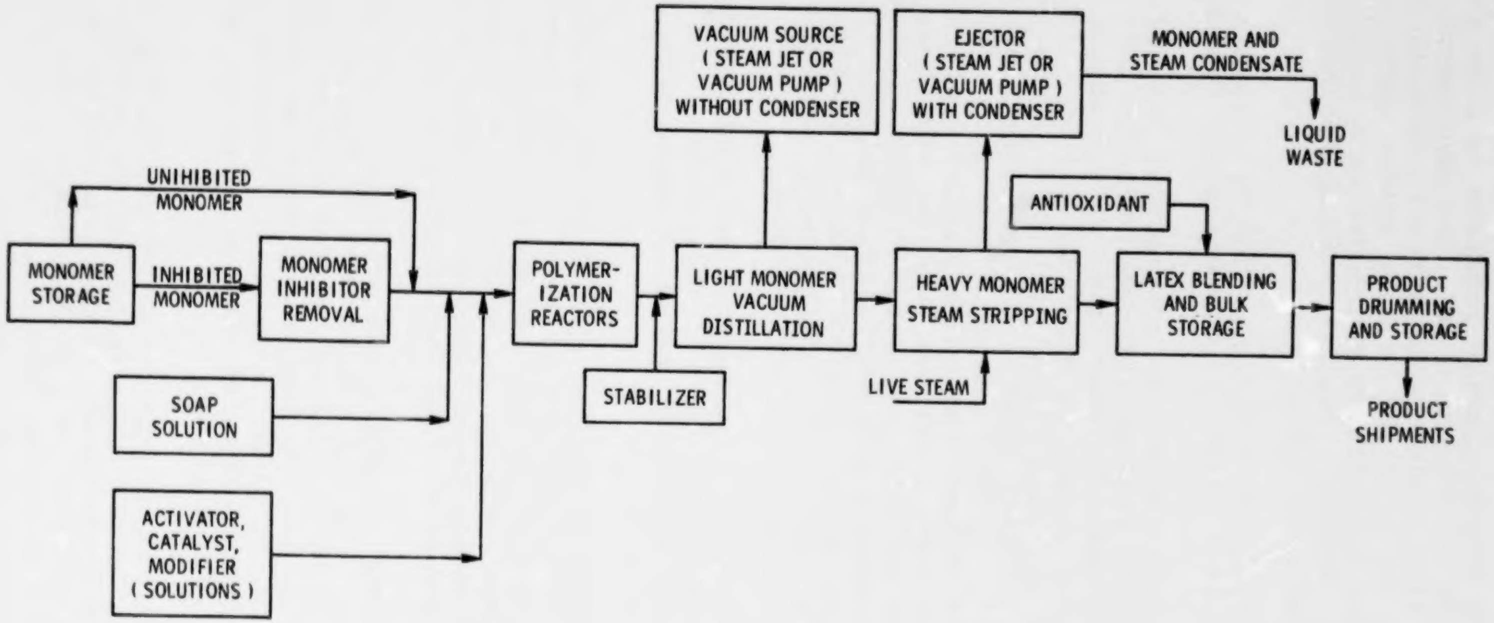
MONOMER STORAGE
UNIHIBITED MONOMER
INHIBITED MONOMER
MONOMER INHIBITOR REMOVAL
SOAP SOLUTION
ACTIVATOR, CATALYST, MODIFIER (SOLUTIONS)
POLYMER- IZATION REACTORS
STABILIZER
LIGHT MONOMER VACUUM DISTILLATION
VACUUM SOURCE (STEAM JET OR VACUUM PUMP) WITHOUT CONDENSER
HEAVY MONOMER STEAM STRIPPING
LIVE STEAM
EJECTOR (STEAM JET OR VACUUM PUMP) WITH CONDENSER
MONOMER AND STEAM CONDENSATE
LIQUID WASTE
ANTIOXIDANT
LATEX BLENDING AND BULK STORAGE
PRODUCT DRUMMING AND STORAGE
PRODUCT SHIPMENTS

Figure 2. Schematic flow diagram for latex rubber production by emulsion polymerization (4).

90%. The solution polymerization reaction is also more rapid; it is usually complete in 1 hr to 2 hr. The copolymers produced by this process are like emulsion SBR but with several improved properties. They are reported to have better abrasion resistance, better flex, higher resilience, and lower heat build-up than the emulsion rubbers. However, they tend to be thermoplastic and are not recommended for tire use (8).

Figure 3 is a generalized materials flow diagram for the production of crumb SBR by a solution polymerization system (4).

Monomers as received, containing inhibitors, are first stripped of these compounds by passage through a caustic soda (NaOH) scrubber. The monomers are then freed of extraneous water, using either fractionating towers or molecular sieves. Fresh and recycled solvents are also passed through a drying column to remove water and unwanted light and heavy components which form as byproducts during polymerization. Drying is crucial since ionic solution polymerizations using Ziegler-Natta coordination catalysts are extremely sensitive to polar compounds such as water, oxygen, and certain oxygenated organic species. A few ppm of water are a necessary and controllable maximum in any of the feed streams to the polymerization reactor. Similarly, active hydrogen compounds and certain hydrocarbons (acetylenes, cyclopentadiene, cyclopentene) must be excluded.

The purified solvent (usually hexane) and monomers are next blended to form the "mixed feed." This mixture can be further dried to remove any remaining traces of water using a desiccant column.

The dried mixed feed of solvent plus monomers is then ready for polymerization. Catalysts can be added to the mixed feed just prior to polymerization or they can be fed directly to the reactor. In some cases, catalyst solutions may be premixed with a portion of the monomers under vigorous agitation to enhance activity and to ensure uniform distribution in the reactor.

The blend of solvent, monomer, and catalyst is polymerized in a series of vessels. The exothermic heat of reaction is continuously removed through the use of chilled reactor jackets or internal cooling coils, the latter employing an ammonia refrigerant, chilled brine, or glycol solutions. Temperature control is important to ensure the desired average molecular weight and molecular weight distribution.

At a rubber solids concentration of 8% to 10%, the solution viscosity is at a level beyond which further conversion of monomer to polymer is inadvisable. Thus, the mixture exits the reactor train in the form of a rubber cement. Polymerization is halted by adding a shortstop solution. The stabilized cement is then pumped to storage tanks prior to further processing.

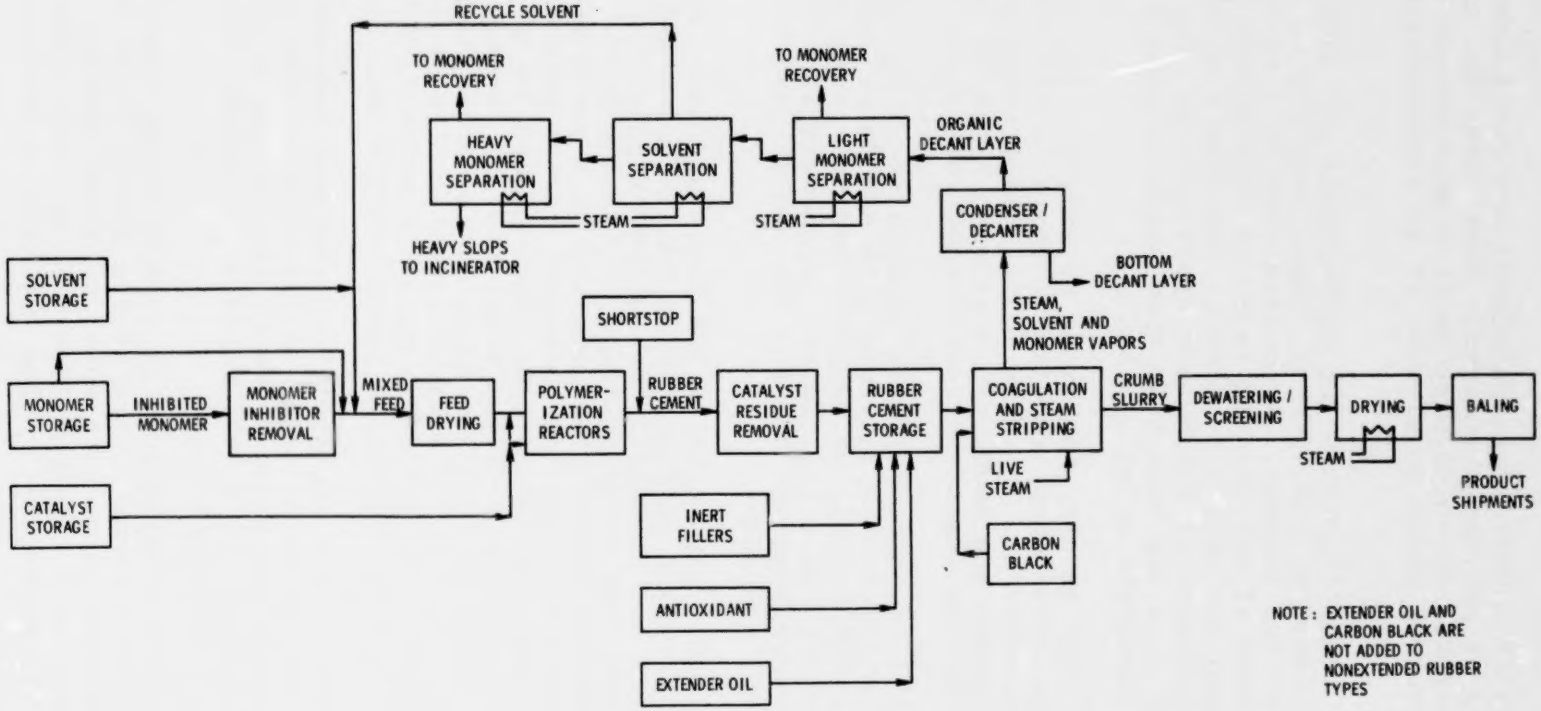

Figure 3. Schematic flow diagram for crumb rubber production by solution polymerization (4).

Excess residues of coordination catalysts are detrimental to the aging stability of polymeric rubbers. Therefore, the undesirable residues are removed as soluble salts in a washing and decanting operation, sometimes using an alcohol or an alcohol/water solution.

At this point, other chemicals and ingredients are added. An antioxidant is added to the viscous rubber solution to prevent deterioration of the polymer. A metered flow of a suitable oil is also added here if the product is to be "oil-extended." Oil-extending reduces the melt viscosity of the rubber to that required for compounding in subsequent applications. The oil is usually blended with the cement at some point between the storage tanks and the steam-stripping operation.

Inert fillers, such as clay, whiting, or barytes, are sometimes added to certain solution-polymerized rubbers to facilitate handling the rubber mixture. In these cases, reinforcing fillers such as carbon black are added, in a process known as "masterbatching," to improve unsatisfactory properties of the rubber.

The rubber cement is pumped from storage to the coagulator where rubber is precipitated in crumb form with hot water under violent agitation. Surfactants may be added to control crumb size and to prevent reagglomeration. In addition to coagulation, this operation partially vaporizes the solvent and the unreacted monomer; these vapors pass overhead.

In the area collectively known as the desolvent area, the resultant crumb slurry passes to steam strippers to drive off the remaining solvent and monomer. The equipment generally consists of either a flash tank or an agitated kettle stripper. Steam, solvent, and monomer vapors pass overhead to a condenser and decanter for recovery. The bottom decant layer, saturated in solvent and monomer, is discharged. The organic layer is sent to a multistage fractionator. Light fractions are removed in the first column. These generally consist of unreacted light monomer; e.g., butadiene. This is usually reclaimed at the monomer supply plant. The second column produces purified solvent, a heavy monomer-water fraction, and other heavy components.

The heavy monomer (i.e., styrene) is condensed, decanted, and recycled. The bottom water layer is discharged. The purified solvent is dried before reuse. The extraneous heavy components stream is waste which can be either decanted before disposal or incinerated as a slop oil.

The stripped rubber crumb slurry is separated and washed with water on vibrating screens. Part of the slurry rinse water is recycled to the coagulator with water or steam makeup. The remaining portion is discharged as overflow. The screened rubber is passed through an extruder-dryer for further dewatering and drying. As the rubber is extruded through a perforated die plate, the mechanical action of the screw heats the material in the barrel to about 143°C. Dewatering and drying could also be accomplished using a rotary filter and a hot-air oven dryer. The dried rubber, usually in the form of pellets, is pressed into 34-kg bales and usually wrapped in polyethylene for storage and shipment.

Reclaimed Rubber (4)--

There currently three different process technologies used by the rubber reclaiming industry in the United States: the digester process, the pan (or heater) process, and the mechanical process. The most common reclaiming technique is the pan process, which has almost replaced the digester process, the oldest of the three. The mechanical process is the least conventional one, and as such, it is not widely practiced. All three processes use similar methods of rubber scrap separation and size reduction. The differences show up in the depolymerization and final processing. Figure 4 is a generalized schematic flow diagram for rubber reclaiming.

Metal Removal, Size Reduction, and Fiber Separation--Scrap rubber received at a reclaiming plant is first sorted to remove steel-belted or studded tires, which can be either sent to special processing facilities or discarded as waste. Brass and steel valve stems and valve seats are manually removed from the remaining tires. The bead wire, which serves to secure the tire to the wheel rim, may also be cut out of the tire at this time.

Next the scrap rubber is size reduced using either crackers or hammer mills. The cracker is a two-roll machine, having working roll lengths of 0.76 m to 1.07 m and diameters of 0.46 m to 0.81 m. Each roll is axially corrugated, and the two rotate in opposite directions at different speeds. As the rubber is dropped into the cracker, the slower roll corrugations momentarily "hold" the waste while the faster roll corrugations shear, slice, crush, and abrade the waste. This process is repeated until all the material passes through a screen of some predetermined mesh size. Some reclaimers undertake futher size reduction down to less than 1.7-mm size (10-mesh) using secondary and tertiary crackers.

A hammer mill is essentially a high-speed rotating drum which hammers the scrap rubber with pivoting "T" or "I" bars or with knives located on the frame within which the drum revolves, with or without a perforated plate or screen that retains the scrap until it is sufficiently size reduced to pass through. The machine containing drum knives may have a special feeding device to control the input of the rubber waste.

Wastes containing reinforcing fiber materials, such as cotton, rayon, nylon, polyesters, fiberglass, and metal, require either

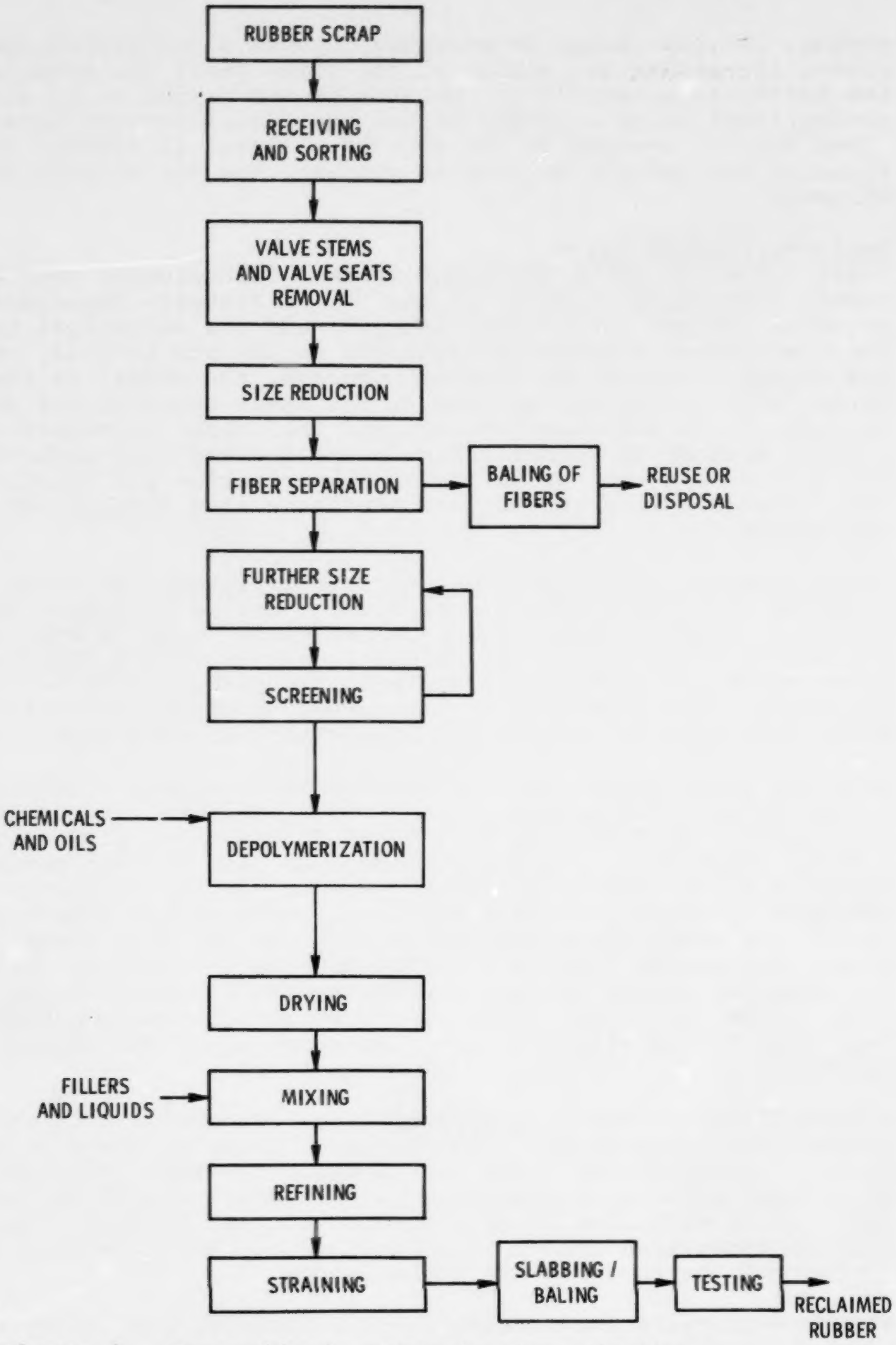

Figure 4. Generalized schematic flow diagram for reclaiming rubber (4).

mechanical fiber separation or chemical fiber degradation. The ground rubber-and-fiber mixture is first separated into streams of different particle size by a screener. These streams are conveyed to separation tables which effectively separate loose fiber from clean rubber by vibration and air flotation. This is a continuous operation with recycle and with free scrap being added at all times.

The fiber and rubber-fiber portions are next fed into hammer mills for hammering or scraping. After the material has been sufficiently size reduced to pass through a peripheral screen, it is fed to sifters or beaters. In these machines, loose rubber particles separate from the fiber and pass through a retaining screen, while the fiber is conveyed for recycle, either to the screener or to another set of hammer mills.

The final operation of the fiber separation process is baling the waste fiber. This baled fiber is made up of small strands, less than 38 mm long, and contains a small amount of entrapped rubber. This fiber is discarded unless there is a market for its reuse.

Fiber-separated rubber is next subjected to fine grinding. Crackers, similar to those used for primary size reduction, grind the rubber to 550 μm (30-mesh) or smaller. Hammer mills can be used for fine grinding but are not as efficient as crackers. The finely ground rubber is then screened. Particles that pass through the screens are ready for depolymerization, while the remaining material is recycled for further size reduction.

Depolymerization--

Digester process--Digestion is a wet process using rubber scrap that has been ground to thicknesses between 6.3 mm and 9.5 mm. The fine, fiber-free rubber particles are mixed with water and reclaiming agents and fed to a jacketed autoclave. These digesters can accommodate about 2,300 kg to 2,700 kg of scrap, water, and chemicals in each reclaim batch. The digester is agitated by a series of paddles on a shaft which is continuously driven at a slow speed to maintain the charge in motion for uniform heat penetration. The digestion liquor is heated by the injection of steam, at pressures generally around 1.38 MPa for a residence time of 8 hr to 12 hr. Reclaiming agents are fed to the digester with the scrap rubber to accelerate depolymerization and to impart desirable processing properties to the rubber. Rubber scrap which has not been mechanically defibered requires chemical degradation during digestion. In such cases, defibering agents and plasticizing oils are added to complete the charge.

When the digestion is complete, the resultant slurry is blown down under internal pressure into a blowdown tank. From there, the rubber slurry is pumped to a holding tank where additional water is added for dilution and washing. After agitation, the mixture is discharged onto vibrating screens where a series of spray nozzles wash the rubber free from the digestion liquor and hydrolyzed fiber. The washed scrap is then passed through a dewatering press. A small amount of residual moisture is necessary to prevent excessive buildup of heat during subsequent refining.

Reclaiming agents that are used in the digester process include petroleum- and coal-tar-based oils and resins as well as various chemical softeners such as di- and trialkylphenol sulfides and disulfides, mercaptans, and amine compounds. Preferred amines include aliphatic long-chain ($C_{10}$to C_{14}) amines and primary amines. Reclaiming agents generally function by catalyzing the oxidative breakdown of polymer chains and sulfur crosslinks. It should be noted that natural rubber can be reclaimed without using reclaiming chemicals.

Sodium hydroxide or calcium chloride and zinc chloride are used as defibering agents in the digester process. The presence of synthetic rubber, such as SBR, necessitates the use of metallic chlorides instead of sodium hydroxide since the latter produces a thermosetting effect with SBR.

Pan (or heater) process--Fiber-separated, fine-ground scrap is reduced to an even smaller particle size by grinding on smooth steel rolls. The rubber is next blended with reclaiming oils in an open mixer and then placed in stacked shallow pans. The depth of treated scrap in these pans may be 150 mm to 200 mm. The stacked pans are placed on a carriage that can be wheeled into a large horizontal heater, which is a single-shell pressure vessel.

In this method of depolymerization, live steam at 1.38 MPa to 1.55 MPa is introduced to the heater to directly contact the rubber scrap. After this treatment, the heater is opened, and the reclaimed scrap is unloaded and cooled. No drying is required because the small amount of water remaining will assist in refining.

Mechanical process--Unlike the other two processes, mechanical reclaiming is continuous. Fiber-separated, fine-ground rubber scrap is fed into a high-temperature, high-shear machine. The machine is a horizontal cylinder in which a screw forces material along the chamber wall in the presence of reclaiming agents and depolymerization catalysts. Temperatures generated are in the range of 177°C to 204°C with time requirements between 1 min and 4 min. The discharged reclaimed rubber needs no drying.

Mixing, Refining, Straining, and Packaging--Reinforcing materials such as clay, carbon black, and softeners are most commonly mixed into the rubber using a horizontal ribbon mixer. This is an enclosed rectangular box with a rounded bottom in which mixing is accomplished by a horizontally driven continuous ribbon, by paddles, or by a combination of the two. The mixed rubber and filler compounds are next intimately blended in a Banbury internal mixer. It usually takes between 1 min and 3 min to blend the material in a single batch. Since extruders permit continuous processing, more reclaimers are converting to that method of blending.

The reclaimed material ("reclaim") next undergoes preliminary refining on a short two-roll mill called a breaker refiner. The smooth rolls are of different diameters and rotate at different speeds so that there is a high friction ratio which tends to form the stock into a smooth clean sheet, approximately 0.3 mm thick. The temperature of the rolls is controlled by water cooling.

The sheet is dropped into a screw conveyor which carries the reclaim to a strainer. The strainer is a heavy-duty extruder which contains a wire screen with 1.7 mm to 370 μm (10-mesh to 40-mesh) openings held between two perforated steel plates in the head of the machine. Straining removes such foreign materials as glass, metal, wood, or sand from the rubber. After straining, the rubber goes on to a second refiner called a finisher, which is the same type of machine as the breaker. The final thickness of the clean reclaim is between 0.05 mm and 0.25 mm.

Each reclaimer may complete his operations by sending his product to the customer in the form of slabs, stacked on pallets, or in bales. Slabs are made by allowing the thin sheet of reclaim to wrap around a windup roll until the proper thickness is obtained. The wrapped layers are then cut off the roll, forming a solid slab of a certain length, width, and weight. Each slab, weighing approximately 14 kg to 16 kg, is dusted with talc to prevent sticking. After quality control approval, the slabs are piled on pallets until the total weight is 680 kg to 910 kg, ready for shipment. As an alternative to the slab process, the reclaim sheet can be air conveyed to a baler, where the rubber is compacted to form a bale of controlled weight. The bales are dusted, bagged, stacked on pallets, tested, and shipped.

Rubber Products Fabrication

Common Feed Materials--

Common feed materials for rubber products fabrication include rubber and rubber latex (including natural, synthetic, and reclaimed material), and various rubber chemicals. Feed materials specific to individual rubber product industries are discussed in the process description for each industry.

Rubber and Rubber Latex--

Natural rubber--Natural rubber is obtained by tapping the tree *Hevea brasiliensis* and collecting latex from which the rubber is separated by a process known as coagulation. Coagulation occurs when various acids or salts are added. The rubber separates from the rubber serum as a white, doughlike mass, which is then milled and sheeted to remove contaminants and to enable drying. This rubber is known as natural rubber. Chemically, it is built of approximately 5,000 isoprene units per molecule in a *cis* (designated herein as cis) configuration. Besides the dry natural rubber, the original latex is also concentrated and transported for use in the production of foam, latex-dipped goods, adhesives, etc.

Natural rubber is mainly used in the United States for truck tires because of its heat-buildup resistance. Other reasons for using natural rubber are its excellent properties and also because rubber making machinery was designed to handle this material. A 1974 total natural rubber consumption of 710,000 metric tons has been reported (9).

Synthetic rubber--The major types of synthetic rubber used in fabricating rubber products and their chemical formulations, properties, and preferred uses are summarized in Table 8 (10-12). Several other elastomers are available. They are considered specialty rubbers and are mostly limited by their cost to use in areas where specific properties are desired. Examples of these elastomers are listed below.

Thiokol (T), polysulfide rubber, has outstanding oil and solvent resistance. However, its other properties are poor.

Silicone rubbers have excellent high and low temperature resistance, good mechanical properties at high temperature, low compression set, and fair oil resistance. Their cost, however, restricts use mainly to aircraft and outer space equipment. Due to their inertness and non-toxicity, the silicone rubbers are also used for some food and surgical applications.

EPR (EPM) is ethylene propylene rubber with good aging, abrasion, and heat resistance. It exhibits excellent resistance to oxygen, ozone, acids, alkalis, and other chemicals over a wide range of temperatures. It is not oil resistant, and its full utilization potential is not fully defined.

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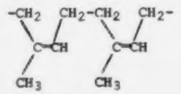
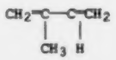
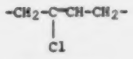
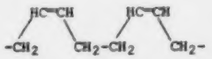
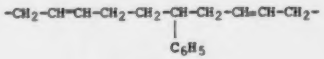
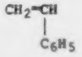
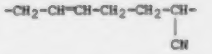
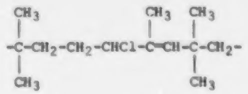
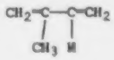
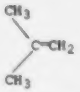
(9) Outlook 1974 - Part II: Status Report on Elastomeric Materials. Rubber World, 169(5):38-46, 1974.

(10) Shreve, N. R. Chemical Process Industries, Third Edition. McGraw-Hill Book Company, New York, New York, 1967. 905 pp.

(11) Kent, J. A. Riegel's Handbook of Industrial Chemistry, Seventh Edition. Van Nostrand Reinhold Company, New York, New York, 1974. 902 pp.

(12) Rosnto, D. V. Injection Molding of Rubber. Rubber World, 166(6):45-61, 1972.

TABLE 8. CLASSIFICATION OF RUBBERS (10-12)

ASTM D 1418 designation	Common or trade name	Chemical designation and formula	Monomer	General properties and use
NR	Natural	 *cis*-1,4-Polyisoprene	None	Excellent physical properties; good resistance to cutting, gouging, and abrasion; low heat, ozone, and oil resistance; poor resistance to petroleum-base fluids. Its use is still preferred in applications that demand elasticity, resilience, tackiness, and low heat buildup. It is indispensable for the treads of tires for buses, trucks, and racing cars. Resilience properties are utilized in engine mounts and suspension units of automobiles. unique applications are in building foundations and bridge bearings.
IR	Polyisoprene		 $CH_2=\underset{\underset{CH_3}{\vert}}{C}-\underset{\underset{H}{\vert}}{C}=CH_2$ Isoprene	Same properties as natural rubber; requires less mastication than natural rubber. The best replacement for natural rubber.
CR	Neoprene	 $-CH_2-\underset{\underset{Cl}{\vert}}{C}=CH-CH_2-$ Chloroprene	$CH_2=CCl-CH=CH_2$ Chloroprene	Excellent oxygen, ozone, heat, tearing, and weathering resistance; good oil resistance; excellent flame resistance, high tensile strength. Wire and cable industries, hose, extruded automobile parts, low-voltage insulation, and protective clothing and linings.
BR	Butadiene	 *cis*-1,4-Polybutadiene	$CH_2=CHCH=CH_2$ Butadiene	Excellent abrasion resistance, resistance to flex cracking, and high resilience; used principally as a blend in other rubbers. Used in tire treads, foams, and footwear.
SBR	SBR (GR-S)	 $-CH_2-CH=CH-CH_2-CH_2-\underset{\underset{C_6H_5}{\vert}}{CH}-CH_2-CH=CH-CH_2-$ Butadiene-styrene	$CH_2=CHCH=CH_2$ Butadiene  $CH_2=\underset{\underset{C_6H_5}{\vert}}{CH}$ Styrene	Good physical properties; excellent abrasion and crack resistance; poor strength, low resilience, low tear strength, poor tack; not oil, ozone, or weather resistant; general purpose rubber used in different proportions with natural rubber for tire treads. It is used for tire carcasses, molded goods, shoe soles, flooring, and insulation.
NBR	Buna N	 $-CH_2-CH=CH-CH_2-CH_2-\underset{\underset{CN}{\vert}}{CH}-$ Butadiene-acrylonitrile	$CH_2=CHCH=CH_2$ Butadiene $CH_2=CHCN$ Acrylonitrile	Excellent resistance to vegetable, animal, and petroleum oils; poor low temperature resistance. Seals, gaskets, rubber rolls, and hoses.
IIR	Chloro-Butyl	 $-\overset{\overset{CH_3}{\vert}}{\underset{\underset{CH_3}{\vert}}{C}}-CH_2-CH_2-CHCl-\overset{\overset{CH_3}{\vert}}{C}=CH-\overset{\overset{CH_3}{\vert}}{\underset{\underset{CH_3}{\vert}}{C}}-CH_2-$ Chloro-isobutylene-isoprene	 Isoprene 	Excellent weathering resistance; low permeability to gases; good resistance to ozone, acids, alkalis, and aging; low tensile strength and resilience; incompatible with natural rubber. Excellent air retention makes it suitable for inner tubes and inner liners of tubeless tires. Also used for many automobile components such as window strips. In its resistance to heat, it plays an indispensable part in tire manufacture forming the hot container for the hot water or steam required to vulcanize the inside of tires. Its good electrical properties and low gas permeability make it suitable for wire and cable insulation, adhesives, coating compositions, and tank lining.

Polyurethane rubber (AU) is a polyurethane diisocyanate with exceptional abrasion, cut and tear resistance, high modulus, and high hardness. It is not suited for normal tire service because abrasion resistance decreases rapidly with increasing temperature. The material is used in some small solid tires, but its main applications are in foams and surface coatings.

Hypalon (CSM) is chlorosulfonated polyethylene with excellent resistance to ozone and strong chemicals like nitric acid, sulfuric acid, chromic acid, hydrogen peroxide, and strong bleaching agents. It has good heat resistance and mechanical properties, limited colorability, fair oil resistance, and poor low temperature resistance. Uses include conveyor belts, steam hose tubes, O-rings and gaskets in ozone generators, miscellaneous molded goods, and coated fabrics for outdoor use.

Fluoroelastomers (FDM) are fluorinated hydrocarbons with excellent high temperature resistance, particularly in air and oil. They are of limited use for cooking utensils.

Reclaimed rubber--The third important feed material in the rubber processing industry is reclaimed rubber, or vulcanized rubber reworked to render it suitable as raw material. Reclaimed rubber is obtained from rubber scrap, natural or synthetic in origin, which is segregated into separate and compatible rubbers and then graded according to quality and intended use. It is not profitable to use reclaimed rubber unless it costs less than half as much as virgin rubber. Its utilization therefore fluctuates depending on the costs of virgin rubbers.

Rubber Chemicals--The commercial application of either raw natural dry rubber or raw synthetic rubber is very limited. For the great majority of users, the rubber must be modified, usually by the addition of chemical agents having specific functions. Exceptions include such uses as crepe rubber shoe soles; cement, as in the familiar rubber adhesives; and adhesives in masking tape.

Raw rubbers and rubber chemicals in prescribed proportions are blended to obtain rubber having the required qualities. The desirable properties achieved by rubber compounding are plasticity, elasticity, toughness, softness, hardness, impermeability, resistance to abrasion, etc. The variety of chemicals added in the compounding step depends on the type of processing that will follow and on final product use. The following is an example of a rubber compound formulation.

Ingredient	Parts by weight
Rubber (such as SBR)	100
Sulfur	2
Zinc oxide	5
Stearic acid	3
Accelerator	1.5
Loading or filling pigment	50
Reclaim, softeners, extenders, colors, blowing agents, antioxidants, antiozonants, odorants, etc.	As required

To identify the materials that are used in the fabrication of rubber products, the following sections present the individual compounds and their functions in rubber processing.

Antioxidants and stabilizers--Antioxidants and stabilizers are needed to protect the rubber during its handling and shipment. Generally, stabilizers are used to protect polymers during their isolation and storage. The antioxidants protect the rubbers both during processing and in the finished product. Most antioxidants give good protection as stabilizers, but not all stabilizers give satisfactory antioxidant activity. Natural rubber needs antioxidants only, but the synthetic polymers require both. Table 9 (13) summarizes the commercially important rubber antioxidants and stabilizers according to the three principal groups: arylamines, phenols, and phenolphosphides. Trade names of these compounds are also given for easier compound identification. Concentration levels of the stabilizers range from 0.5 to 1.25 parts of stabilizer per 100 parts of rubber.

Pigments--Any solid material that is mixed into rubber, except for vulcanizing agents, may be referred to as a pigment. Dry pigments can be classified as either reinforcing agents or filling materials. The reinforcing agents improve the properties of the vulcanizates; the filling agents serve as diluents. Commonly used pigments and their average particle sizes are given in Table 10. For example, every part of rubber used in tire treads may contain 0.1 part of carbon black; tubes require even more, and carcasses require only slightly less.

In the prepration of colored stocks, a sufficient quantity of a background pigment with high hiding power (e.g., titanium pigments) and organic dye are added to give the desired color. For preparation of less bright shades, inorganic pigments such as iron oxide, antimony sulfide, chromiun sulfide, chromium oxide, cadmium selenide, and ultramarine blue are used. Basic requirements for colored pigments depend on their stability during

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(13) Kirk-Othmer Encyclopedia of Chemical Technology, Second Edition, Vol. 17. John Wiley & Sons, Inc., New York, New York, 1968. 884 pp.

TABLE 9. COMMERCIAL ANTIOXIDANTS (13)

Chemical name	Trade names or trademarked names
Aldehyde-amine type	
Aldol-1-naphthylamine	AgeRite Resin, Aceto AN
Butyraldehyde-aniline product	Antox
Acetaldehyde-aniline product	Crylene
Aldol-aniline product	Resistox
p,*p*'-Diaminodiphenylmethane	Tonox
Ketone-amine type	
1,2-Dihydro-2,2,4-trimethylquinoline resin	AgeRite Resin D, Flectol H, Aceto POD
1,2-Dihydro-2,2,4-trimethyl-6-ethoxyquinoline	Santoflex AW, Polyflex
1,2-Dihydro-2,2,4-trimethyl-6-phenylquinoline	Santoflex B
1,2-Dihydro-2,2,4-trimethyl-6-dodecylquinoline	Santoflex DD
Diaryldiamine type	
N,*N*'-diphenyl-*p*-phenylenediamine	AgeRite DPPD, JZF
N,*N*'di-β-naphthyl-*p*-phenylenediamine	AgeRite White, Aceto DIPP
N,*N*'-dialkylphenyl-*p*-phenylenediamine	Wingstay 100, Wingstay 200
Diarylamine type	
Phenyl-1-naphthylamine	Neozone A, Aceto PAN
Phenyl-2-naphthylamine	Neozone D Special, AgeRite Powder, PBN, Aceto PBN
Alkylated diphenylamine	AgeRite Stalite, Octamine, Pennox A, Wytox ADP, Polylite
Ketone-diarylamine type	
Diphenylamine-acetone, high-temperature product	AgeRite Superflex, BLE-25, Neozone L, Cyanoflex 100
Diphenylamine-acetone, low-temperature product	Aminox
Phenyl-2-naphthylamine-acetone, low-temperature product	Betanox Special
Diphenylamine-acetone-aldehyde product	BXA
Substituted phenol type	
2,6-Di-*t*-butyl-4-methylphenol	CAO-1, DBPC, Tenamene 3, Ionol, Amoco 533, Dalpac 4, Deenax, Tenox BHT, CAO-3
Butylated hydroxyanisole	Tenox BHA, Sustane BHA
2-α-Methylcyclohexyl-4,6-dimethylphenol	Nonox WSL
Styrenated phenol	AgeRite Spar, Wingstay S, Styphen 1
Hindered phenol	Wingstay T, Nevastain A, Cyanox LF, Santowhite 54
Butylated styrenated *m*,*p*-cresol	Wingstay V
Bisphenol type	
4,4'bis(2,6-*t*-Butylphenol)	Ethyl 712
2,2'-Methylenebis(4-methyl-6-*t*-butylphenol)	Plastanox 2246, CAO-5
2,2'-Methylenebis(4-ethyl-6-*t*-butylphenol)	Plastonox 425
4,4'-Methylenebis(6-*t*-butyl-2-methylphenol)	Ethyl 720
4,4'-Methylenebis(2,6-di-*t*-butylphenol)	Binox M, Ethyl 702, Ionox 220
4,4'-Butylidenebis(6-*t*-butyl-3-methylphenol)	Santowhite powder
2,2'-Thiobis(4-methyl-6-*t*-butylphenol)	CAO-4
4,4'-Thiobis(6-*t*-butyl-2-methylphenol)	Ethyl 736
4,4'-Thiobis(6-*t*-butyl-3-methylphenol)	Santowhite Crystals
4,4'-Thiobis(3,6-di-*sec*-amylphenol)	Santowhite L
Hindered bisphenol	AgeRite Superlite, Naugawhite, Pennox D
4,4'-Dioxydiphenyl	Antioxidant DOD
Alkylated polyphenol	Wingstay L
Hydroquinone type	
Hydroquinone	Tecquinol
Monobenzyl ether of hydroquinone	AgeRite Alba
2,5-Di-*t*-amylhydroquinone	Santovar A
Aminophenols	
N-butyl-*p*-aminophenol	Tenamene 1
N-lauroyl-*p*-aminophenol	Suconox 12
2,6-Di-*t*-butyl-α-dimethylamino-4-methylphenol	Ethyl 703
4-Isopropoxy diphenylamine	AgeRite Iso
Phosphite type	
Modified high-molecular-weight hindered phenol phosphite	AgeRite Geltrol
Tri(nonylphenyl)phosphite	Polygard
2-Ethylhexyl octylphenylphosphite	VC-1

product cure and the requirements of the final product itself. Other pigments that may be used for specific purposes include: fibrous asbestos, for its stiffening effect and heat resistance; cotton or other textile fibers, for the same purpose, but with less heat resistance; graphite, to produce a lower friction coefficient; ground cork, for compounds needing low density; glue, as a stiffener; litharge or other lead pigments, where high density is required for opacity to x-rays; and stiffening resins, such as polyvinyl chloride, phenolformaldehyde resins, polystyrene, or high-styrene/low-butadiene copolymer resins.

TABLE 10. PIGMENTS USED IN RUBBER COMPOUNDING (13)

Pigment	Grade or trademark and company	Average particle diameter, nm
Carbon black	CC	10 to 20
	S301(MPC)	25 to 30
	S300(EPC)	30 to 33
	N440(FF)	36
	N601(HMF)	50 to 60
	N770(SRF)	70 to 90
	N880(FT)	150 to 200
	N990(MT)	250 to 500
	Acetylene	43
Whiting	Witco AA (Witco Chemical Co., Inc.)	3,900
	Micronized (The Glidden Co.)	1,500
	Witcarb R-12 (Witco Chemical Co., Inc.)	145
	Witcarb R (Witco Chemical Co., Inc.)	50
	Purecal V (Wyandotte Chemicals Corp.)	40
	Purecal M (Wyandotte Chemicals Corp.)	1,500
	Atomite (Thompson, Weinman)	1,500
	Calcene TM (PPG Industries)	100
Clay	Catalpo (Freeport Kaolin)	800
	Dixie (R. T. Vanderbilt Co., Inc.)	1,000
Silica	Hi-Sil (PPG Industries)	25
Calcium silicate	Silene EF (PPG Industries)	30

Softeners, extenders, and plasticizers--A wide variety of oils, tars, resins, pitches, and synthetic organic materials are used as softeners in rubber compounding. These compounds do not necessarily have any relation to the softness of the compounded material. The softeners are used to decrease the material viscosity for improved workability, reduce mixing temperature, increase tack and stickiness, aid in dispersion of pigments, reduce shrinkage, provide lubrication, and improve extrusion or molding characteristics and the like. The term extended is applied to materials that replace a portion of the rubber, usually with some processing advantage. Both of these materials can also be used as diluents.

Plasticizers are primarily used to lower the viscosity of the uncured stock rubber during milling. They should not affect the rate of vulcanization or properties of the cured rubber. The ease of plasticization corresponds with the ease of oxidation, which is in the following order: natural rubber > polyisoprene > polybutadiene > polystyrene > polychloroprene > nitrile rubber. The concentration of plasticizers applied to natural and synthetic rubbers may range from 0.25 part to 1.5 parts per 100 parts of rubber material. The plasticizers are effective in natural rubber, polyisoprene, and SBR. The other synthetic rubbers are less affected by the presence of a plasticizer.

The best softeners are those which are good solvents for the rubber. Table 11 lists some softeners and plasticizers used in the processing of natural and synthetic rubber.

TABLE 11. TYPICAL SOFTENERS AND PLASTICIZERS USED IN RUBBER COMPOUNDING (13)

Rubber type	Softener/plasticizer
Natural rubber (SBR)	All petroleum fractions Pine tars and resins Coal tar fractions Pentachlorothiophenol (RPA-6, Renacit VI) and its activated zinc salt (Endor) Thioxylenols (Pitt-Consol 640) 2,2'-Dibenzamidodiphenyldisulfide (Pepton 22) Zinc 2-benzamidothiophenoxide (Pepton 65)
Neoprene (CR)	Naphthenic petroleum fraction Coal tar fractions Esters Dioctyl sebacate Butyl oleate Monomeric polyether Triethylene glycol caprylatecaprate Trioctyl phosphate
Nitriles (Buna N)	Coal tar fractions Monomeric esters Adipates Sebacates Tributoxyethyl phosphate monomeric fatty acid ester (Synthetics L-1) Di(butoxyethoxyethyl)adipate (TP-95) Triglycol ester of vegetable oil fatty acid (Plasticizer SC) Coumarone - indene resins Rosins Modified phenolics Tetrahydronaphthalene Dibutyl phthalate Dibutyl sebacate
Butyl rubber (IIR)	Mineral oils Paraffin wax Petrolatum Paraffinic and naphthenic oils

Vulcanization and acceleration agents--When rubber is mixed with sulfur and heated, vulcanization (cure) occurs. The terms cure and vulcanization are interchangeable and may be defined as the chemical reaction which combines the polymer molecules of rubber by crosslinking into larger molecules, restricting their further movement. Vulcanization changes the rubber to a strong elastic substance which is tack free, abrasion resistant, and not readily soluble in common solvents. Sulfur is the vulcanization agent that has been used during the whole period of rubber's existence. Regardless of how little or how much sulfur is used in vulcanizing, some sulfur remains uncombined; it is known as free sulfur. High sulfur materials that liberate sulfur at vulcanizing temperatures, such as organic polysulfides, may be substituted for sulfur. Examples of these compounds are tetramethylthiuram disulfide (Methyl Tuads), tetraethylthiuram disulfide (Ethyl Tuads), dipentamethylenethiuram tetrasulfide (Tetrone A), 4,4'-dithiodimorpholine (Sulfasan R), selenium diethyldithiocarbonate (Selenac), aliphatic polysulfide polymer (Thiokol VA-7), and alkylphenol disulfides (Vultac 2,3).

Because some rubbers contain no unsaturation, they must be vulcanized using different chemicals and techniques, such as peroxides or radiation. Another class of curing agents is found among the organic peroxides, such as di-*tert*-(designated herein as tert) butyl and dicumyl peroxides for SBR and silicone rubbers. Terpolymers containing a known nonconjugated diene have been developed and can use sulfur for vulcanization. Neoprene rubber is vulcanized using zinc oxide and magnesium oxide. Butyl rubber may be vulcanized using alkylphenol formaldehyde resins. Oxides of certain metals such as lead and zinc are used to accelerate the vulcanization.

Use of elemental sulfur as the vulcanizing agent requires the addition of auxiliary materials to supply the desired properties. The organic accelerator is the most important of these materials. The accelerator has a strong influence on processing safety, the rate of vulcanization, and the physical properties of sulfur-vulcanized rubber. Accelerators are listed in Table 12.

Antiozonants--As their name suggests, antiozonants are used to protect rubber from the effects of ozone. Ozone can cause severe cracking in rubber articles, particularly under stress. For example, rubber insulation used around electrical equipment, UV lamps, and neon lights must contain antiozonants because of the high ozone concentrations present. As a result of ozone attack on rubber, there is a loss of double bonds. Consequently, highly unsaturated rubbers (natural and styrene-butadiene) are most easily attacked. The antiozonants appear to work by forming a protective film between the rubber and the ozone atmosphere. Commercial antiozonants used for rubber protection are listed in Table 13.

TABLE 12. COMMERCIAL ACCELERATORS (13)

Chemical name	Trade names or trademarked names
Aldehyde-amine reaction products	
Acetaldehyde/ammonia	Acetaldehyde Ammonia, Aldehyde Ammonia
Formaldehyde/ethyl chloride/ammonia	Trimene Base
Butyraldehyde/butylamine	Accelerator 833
Butyraldehyde/aniline	Accelerator 808, A-32, Beutene, Goodrite Pullman
Butyraldehyde/acetaldehyde/aniline	A-100
Formaldehyde/*p*-toluidine	Accelerator 8
Acetaldehyde/aniline	Ethylidene Aniline
Heptaldehyde/aniline	Hepteen Base
2-Ethyl-2-hexenal/aniline	Phenex
Hexamethylenetetramine	Aceto HMT, Methenamine NF
Arylguanidines	
Diphenylguanidine	DPG
Di-*o*-tolylguanidine	DOTG
Triphenylguanidine	Triphenylguanidine
Mixed diarylguanidines	Accelerator 49
Diphenylguanidine phthalate	Guantal
Di-*o*-tolylguanidine salt of dicatechol borate	Permalux
Dithiocarbamates	
Copper dimethyl-	Cumate
Lead dimethyl-	Ledate
Bismuth dimethyl-	Bismate
Zinc dimethyl-	Methyl Zimate, Methyl Ziram, Methazate, Accelerator L, Eptac 1, Aceto ZDMD, Vulcacure ZM
Selenium dimethyl-	Methyl Selenac
Zinc diethyl-	Ethyl Zimate, Aceto ZDED, Cyzate E, Ethazate, Ethyl Ziram
Zinc dibutyl-	Butyl Zimate, Butazate, Butyl Ziram, Cyzate B, Aceto ZDBD
Zinc dibenzyl-	Arazate
Selenium diethyl-	Ethyl Selenac, Ethyl Seleram
Tellurium diethyl-	Tellurac
Piperidinium pentamethylene-	Accelerator 552
Potassium pentamethylene-	Accelerator 89
Zinc pentamethylene-	ZPD-Henley
Cadmium diethyl-	Ethyl Cadmate
Sodium dibutyl-	Butyl Namate, Pennac SDB, Tepidone, Vulcacure NB
Thiuram sulfides	
Tetramethylthiuram monosulfide	Thionex, Aceto TMTM, Cyuram MS, Unads, Monex, Mono Thiurad, TMTM-Henley
Tetrabutylthiuram monosulfide	Pentex
Tetramethylthiuram disulfide	Aceto TMTD, Cyuram DS, Methyl Thiram, Methyl Tuads, Thiurad, Thiuram M, Tuex, Vulcacure TMD, Royal TMTD
Tetraethylthiuram disulfide	Aceto TETD, Ethyl Thiram, Ethyl Thiurad, Ethyl Tuads, Ethyl Tuex, Thiuram E
Dipentamethylenethiuram tetrasulfide	Tetrone A, Sulfads
Dimethyldiphenylthiuram disulfide	Accelerator J
Thiazoles	
2-Mercaptobenzothiazole	MBT, Captax, Rotax, Mertax, Royal MBT, Thiotax, Akron MBT
Zinc benzothiazolyl mercaptide	Zetax, ZMBT, Pennac ZT, Vulcacure ZT, O-X-A-F, Bantex, Zenite
2,2'-Dithiobis(benzothiazole)	MBTS, Altax, Thiofide, Royal MBTS, Akron MBTS
2-Benzothiazyl-*N*,*N*-diethylthiocarbamyl sulfide	Ethylac
Sulfenamides	
N-*t*-Butyl-2-benzothiazole-	Santocure NS
N-Cyclohexyl-2-benzothiazole-	Cydac, Comac S, Santocure, Delac S, Durax, Royal CBTS
N,*N*'-Diisopropyl-2-benzothazole-	DIBS, Dipac
N-Oxydiethylene-2-benzothiazole	AMAX, NOBS Special, Santocure MOR
N-(2,6-dimethylmorpholine)-2-benzothiazole-	Santocure 26
N-Diethyl-2-benzothiazole-	Accelerator AZ
Miscellaneous	
Trimethylthiourea	Thiate E
Trialkylthiourea	Thiate G
1,3-Diethylthiourea	Pennzone E
1,3-Bis(2-benzothiazolylmercaptomethyl)urea	El-Sixty
2-Mercaptothiazoline	2-MT

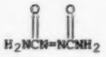
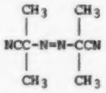
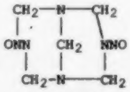
TABLE 13. COMMERCIAL ANTIOZONANTS (13)

Chemical name	Trade names or trademarked names
Symmetrical diamines	
N,N'-di-*sec*-butyl-*p*-phenylenediamine	Eastozone 2, Gasoline AO-22
N,N'-dimethyl-N,N'-bis(1-methylpropyl)-*p*-phenylenediamine	Eastozone 32
N,N'-bis(1-ethyl-e-methylpentyl)-*p*-phenylenediamine	Eastozone 31, UOP 88, Antozite 2, Santoflex 17
N,N'-bis(1-methylheptyl)-*p*-phenylenediamines	Eastozone 30 UOP 288, Santoflex 217, Antozite 1
Mixture of dialkylaryl-*p*-phenylenediamines	Wingstay 100, Wingstay 200
N,N'-bis(1,4-dimethylpentyl)-*p*-phenylenediamine	Eastozone 33, Antozite MPD, Santoflex 77
Unsymmetrical diamines	
N-isopropyl-N'-phenyl-*p*-phenylenediamine	Flexzone 3-C, Santoflex 36, Cyzone IP, Eastozone 34, Nonox ZA, A.O. 4010 NA
N-phenyl-N'-cyclohexyl-*p*-phenylenediamine	Flexzone 6-H, Santoflex 66, A.O. 4010
N-phenyl-N'-*sec*-butyl-*p*-phenylenediamine	Flexzone 5-L
N-phenyl-N'-(1,3-dimethylbutyl)-*p*-phenylenediamine	Antozite 67, Flexzone 7-L, Santoflex 13, UOP 588, Wingstay 300
N-phenyl-N'-*sec*-octyl-*p*-phenylenediamine	UOP 688
Other types	
1,2-Dihydro-2,2,4-trimethyl-6-ethoxyquinoline	Santoflex AW, Polyflex
Nickel dibutyldithiocarbamate	NBC
Nickel isopropylxanthate	KPNI
Waxes	

Other rubber chemicals--

Blowing agents--Blowing agents are used to produce cellular rubber (foam). They must be finely dispersed and of fine size to give uniform pore-size product. The cellular structure is formed by gases which are either generated within the compound during vulcanization or dissolved in a compound under pressure. Examples of blowing agents include sodium bicarbonate, sodium carbonate, ammonium bicarbonate, and ammonium carbonate. Some organic materials which release nitrogen are also in use; they are listed in Table 14.

TABLE 14. BLOWING AGENTS WHICH RELEASE NITROGEN (13)

Chemical name	Formula	Trade name
Azodicarbonamide	 $H_2NC(=O)N{=}NC(=O)NH_2$	Celogen AZ, Genitron AC, Kempore R-125, Porofor K-1074
Azoisobutyronitrile	 $NCC(CH_3)_2{-}N{=}N{-}C(CH_3)_2CN$	Genitron AZDN, Porofor N, Aceto AZIB, Warecel 70
Diazoaminobenzene	$C_6H_5NHN{=}NC_6H_5$	Porofor DB, diazoaminobenzene
Azocyclohexylnitrile	$C_6H_{10}(CN)N{=}N(CN)C_6H_{10}$	Genitron CHDN
N,N'-dinitrosopentamethylenetetramine		Unicel ND, DNPT, Opex, Vulacel
N,N'dimethyl-N,N'-dinitrosoterephthalamide	$C_6H_4(CON(NO)CH_3)_2$	Nitrosan
Benzenesulfonyl hydrazide	$C_6H_5SO_2NHNH_2$	Genitron BSH, Porofor BSH
Benzene-1,3-disulfonyl hydrazide	$C_6H_4(SO_2NHNH_2)_2$	Porofor B-13
p,*p*'-Oxybis(benzenesulfonyl hydrazide)	$O(C_6H_4SO_2NHNH_2)_2$	Celogen, Genitron OB, Porofor DO-44
Diphenylsulfon-3,3' disulfonyl hydrazide	$SO_2(C_6H_4SO_2NHNH_2)_2$	Porofor D-33
4,4'-Diphenyldisulfonyl azide	$(C_6H_4SO_2N_3)_2$	Nitropore CL-100

Organic activators--In some cases, even the addition of an accelerator results in a slow rate of rubber cure. This rate can be increased by incorporation of organic activators. Examples of these compounds are given in Table 15.

Retarders--Prevention of premature cure during the processing of rubber stock is important if fast accelerators are used to prevent rubber scorching. Some of the retarding agents are listed in Table 16.

TABLE 15. ORGANIC ACTIVATORS (13)

Composition	Trade name
Primary fatty amines	Alamine 7,46
Mono- and dibenzylamines	DBA
Diphenylguanidine phthalate	Guantal
Zinc salts of a mixture of fatty acids	Laurex
Mixture of organic and inorganic acetates	MODX
Dibutyl ammonium oleate	Barak
Normal lead salicylate	Normasal
Fatty acids and metal soaps	

TABLE 16. COMMONLY USED RETARDERS (13)

Chemical name	Trade name
Phthalic anhydride	Retarder E-S-E-N
Benzoic acid	
Salicylic acid	
Maleic acid	
Maleic anhydride	
Terpene-resin acid blend	Turgum S
N-nitrosodiphenylamine	Goodrite Vultrol, Retarder J, Redax

Common Operations--
The large number of products made of rubber and rubber latex required the development of many specific approaches to shape the product (hose, belt, molded goods), combine it with other materials (fabric, wire), or produce proper rubber consistency (hard rubber, foam, sponge). These approaches vary, based on product specifications. In general, however, all rubber product fabrication processes consist of 1) preparation of a rubber or latex compound; 2) forming the compound into the desired shape (calendering, molding, extrusion, dipping), and 3) product vulcanization or curing.

Compounding--One of the most important stages in rubber processing is compounding (mixing). It governs the quality of the final product since all the process steps that follow depend on an adequate and uniform mix. Mixing must provide 1) a uniform blend of all the constituents of the mix, 2) an adequate dispersion of the pigments, and 3) uniformity in consecutive batches for smooth further processing. Mixing can be carried out on a two-roll mixer or an internal mixer such as the Banbury mixers. All of these mixers are designed for batch operation.

The batch size processed on a mill can very depending on mixing equipment capacity. Mills are available with roll sizes ranging from 0.35 m to 1.07 m. The smaller sizes are more popular due to the better batch control they provide. Mixing equipment capacity ranges from 68 kg to 136 kg for a 2.3-m mill and 454 kg or more for the largest internal mixers.

The roll mill consists of two parallel horizontal rolls rotating in opposite directions at slightly different speeds. The rubber is worked by being pulled through the nip. The temperature in the roll mill is controlled by passing cold or hot water, steam, or hot oil through the hollow rolls. The nip width is adjustable. Rubber comes out of the roll mill as a sheet, which is cut to proper size before further use.

The internal mixer such as the Banbury is a more effective device for rubber compounding. It consists of a completely enclosed mixing chamber in which two spiral-shaped rotors operate, as illustrated in Figure 5 (14).

Rubber is fed through a hopper. The two rotors rotate in opposite directions at slightly different speeds and are hollow to allow circulation of water or steam for temperature control. The product mix from the internal mixer is discharged into a two-roll mill, producing rubber sheets. To obtain good mixing, carefully selected individual ingredients must be added in a specific order because some materials mix with rubber better than others do.

After the raw rubber has been passed between the heated mill rolls a few times, it becomes sufficiently soft to adhere to the front, slower moving roll. The distance between rolls is then adjusted so that there is a "bank" of rubber in the "bite" of the rolls. When the rubber is sufficiently soft, additional compounding ingredients are spread on the rubber on the bank. The rubber is cut and covered over to aid in dispersing the individual materials throughout the batch.

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(14) McPherson, A. T., and A. Klemin. Engineering Uses of Rubber. Reinhold Publishing Corporation, New York, New York, and Chapman & Hall, Ltd., London, United Kingdom, 1956. 490 pp.

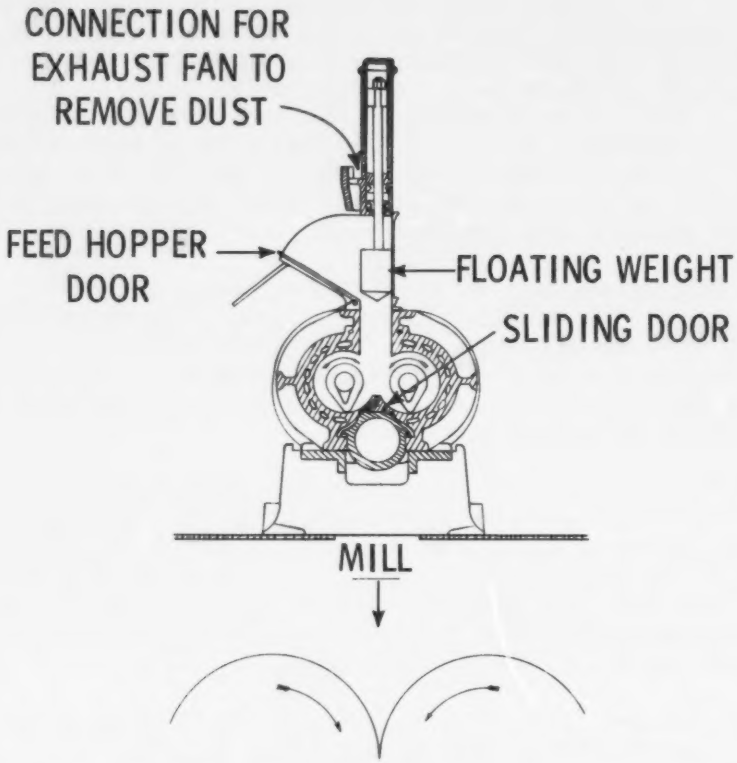

Figure 5. Cross section of a Banbury internal mixer mounted over a rubber mill (14).

Internal mixers can handle large batches in relatively short periods of time. However, they are not suitable for the addition of sulfur because their high operating temperature could cause premature vulcanization or scorching. Consequently, even though most of the compound ingredients are added to the internal mixer, the sulfur is added in a subsequent operation on a roll mill.

Forming--The rubber slabs obtained from the mixing mills may be immediately cut into disks or rectangular pieces suitable for charging into a mold. The consistency of the compound often determines how the rubber will be processed and what equipment can be used for building or making up rubber articles. Most of the mixed rubber must be processed into a form suitable for further fabrication. Processes utilized here include calendering, extrusion, frictioning, spreading, slabbing, and cutting.

Calendering--A calender usually consists of three hollow revolving rolls placed one above the other in such a way that the spacing between them can be accurately adjusted. The temperature on the rolls can be controlled by circulation of steam or cold or hot water through the hollow rolls. The rolls can be driven either at the same or different speeds. A typical calendering process is schematically shown in Figure 6.

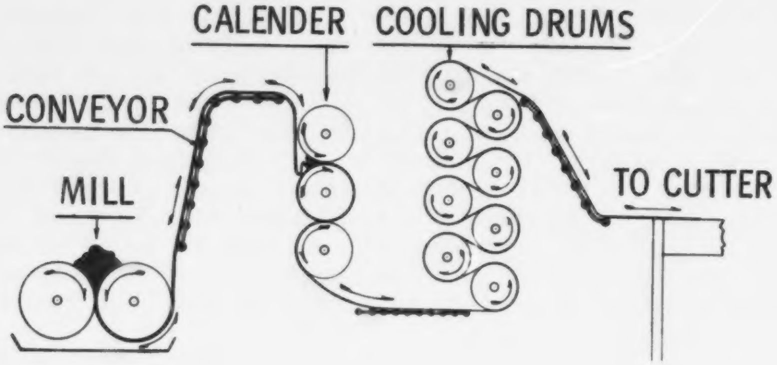

Figure 6. Diagram of the calendering process (14).

The purpose of calendering is to form smooth sheets of rubber compound of accurate thickness; it can also be used to coat or impregnate fabric. Coating operations are performed in either three- or four-roll calenders. The three-roll calender applies a coating to one side of the fabric; the four-roll calender coats both sides of the fabric.

When using fabric is required for reinforcement, as in hose and belting, fabric-inserted diaphragms, and tires and footwear, the fabric is usually rubberized by passing it through a friction calender along with the rubber compound. In fabric frictioning, the center roll of the calender is run hotter and faster than the top and bottom rolls. This forces the rubber into the mesh of the fabric.

Fabric is sometimes rubberized by spreading on the fabric surface a heavy dough prepared by blending a suitable rubber compound with gasoline or other solvent. The fabric is stretched and the dough is applied in a thin, uniform layer by means of a knife mounted perpendicular to the fabric. When the spreading is completed, the fabric is passed slowly over heating coils to evaporate the solvent. The spreading process is applicable to cases in which either the fabric or the compound is not adaptable to the friction process.

Rubber compound obtained from calendering may be used in a variety of applications in many different shapes. Calendered rubber may be automatically cut into strips as it comes from the cooling drums, die-cut to any desired shape by means of a clicking machine, or cut to desired lengths by means of a water-lubricated circular cutter.

Extrusion--The process of extrusion involves forcing the rubber compound through an extrusion machine. These machines can operate with either a cold or a warm rubber feed. Cold feed extruders are longer than the warm feed type in order to permit sufficient breakdown of the rubber compounds for smooth extrusion. Basically, a power driven screw forces the rubber through a cylinder to the front of the machine where it is forced through a die. The extrusion cylinder as well as the screw may be equipped with cooling water or steam for temperature control. Any number of dies are available to provide the desired extruded shapes. Since the rubber expands after being pushed through the die, the die must be smaller in size than the desired resulting extruded article. The extruder may be fed by hand or by a force-feed system consisting of two feed rollers. Newer extruders operate under vacuum to eliminate trapped air and moisture.

Extrusion is a very economical and widely used method of processing rubber, both for making blanks for molding and for forming rods, tubes, strips, channels, and gaskets in a wide variety of sizes and shapes. The operation sequence in the extrusion process is shown in Figure 7 (14).

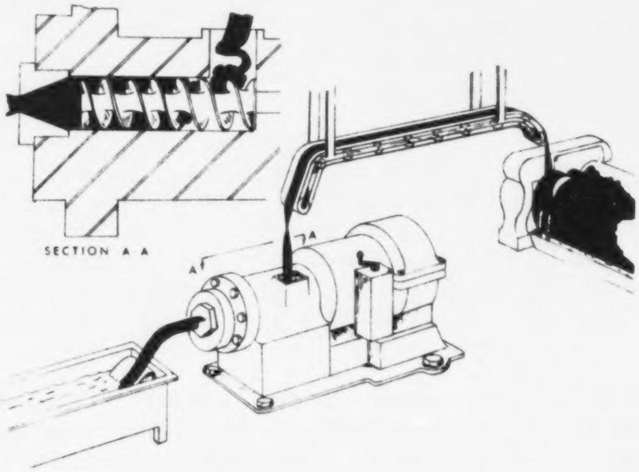

Figure 7. Extrusion processes (14).

When it is intended to employ a compound as insulation or jacket on a wire, or as a cover on a previously prepared hose carcass, a side delivery head is used on an extrusion machine. In this case, a wire or a hose carcass is fed through the head in a direction perpendicular to the axis of the extruder screw. The head is designed so that the compound is deflected 1.57 rad (90°) and completely surrounds the wire or hose carcass.

Some rubber articles may be produced directly by cutting the milled rubber stock; e.g., if large pieces of heavy gauge rubber stock are needed as blanks for molded rubber articles, they are cut from mixing mill stock (made into a slab of the proper thickness) by means of a knife and a template. Similarly, tubed or extruded compound is cut as needed using cutting machines which may be synchronized with the extruder.

Vulcanization (curing)--Vulcanization of rubber products is done at elevated temperatures (100°C to 200°C for 10 min to 30 min) and can be carried out under numerous conditions. Some articles are cured during the manufacturing step if sufficient heat is generated in the process (e.g., molded products); other articles require a separate curing step (e.g., latex products and tires).

Mold Curing--Molded rubber parts are formed and vulcanized in a single operation by the simultaneous application of pressure and heat. Compression is the oldest type of molding and consists of placing preshaped rubber into a mold and closing the mold under pressure; this causes the rubber to fill out into the mold cavity. The heat from the heated platens of the press is conducted through the mold and vulcanizes the rubber. The platens are usually heated by circulating steam through holes drilled in them. Occasionally, electricity or gas burners are used for this purpose.

The rubber overflow or flash must be removed from the article. This operation is labor intensive and thus expensive because it requires hand labor. If possible the rubber parts are dipped in dry ice, causing the thin rubber flash to become brittle and easily broken off. This method can be used only if the main body of the part is large enough not to become cool and inflexible and if the rubber is not freeze resistant.

In transfer molding, the uncured rubber stock is transferred from one place to another within the mold, allowing the manufacture of complex shapes and articles containing metal inserts. Transfer molding permits closer dimensional control and generally reduces flash. Normally the rubber is placed in a transfer cavity which is fitted with a ram or piston. The force applied to the ram or piston and the heat from the mold cause the rubber to be softened and spread in the molding cavity and cured at the same time.

Injection molding is similar to transfer molding except that the soft rubber compound is injected into the molds. A screw mechanism is utilized to force unvulcanized rubber into a tightly closed mold. Forcing the rubber through small passages under high pressure increases the temperature of the injected compound and cures the rubber. In order to make injection molding profitable, very short cycles are required, generally in the 45-s to 90-s range. These short times require a curing temperature of 204°C.

In molding thick articles, long curing times are needed because of the low thermal conductivity of the rubber. This problem is partially overcome by dielectric heating of the blank before it is placed in the mold. This heating also improves the flow of the compound in the mold.

An example of more complicated molding is that of the pneumatic tire in which a steel mold shapes the exterior surface of the tire from bead to bead, and the pressure during cure is supplied from a flexible bag acting as a diaphragm that forces the uncured tire against the mold surface. The diaphragm, an integral part of the press, is made of a resin-cured butyl stock which has extremely good heat resistance. Steam or hot circulating water is introduced to the inside of the diaphragm to cure the tire from the outside. (Tire vulcanization is further described in this section.)

Curing of other rubber articles--Extruded articles and some molded articles may require additional curing. The most common method of vulcanizing these articles is to place them in pans that are set on a truck and rolled into a large steam chamber or heater for vulcanization. Varnish or lacquer may be applied before vulcanization to produce a smooth, glossy product finish.

If curing at elevated pressure is desired, water is used in place of steam. Rubber-lined vessels are steam cured unless they are too large to fit in a steam autoclave. Boiling water is used in such cases.

Air is sometimes preferred over steam in the vulcanization step, especially when moisture must be avoided, or staining or water spotting must be prevented. Hot air at either atmospheric or elevated pressure (103.4 kPa to 275.8 kPa) is usually used. The air is circulated at a rapid rate to provide even heating of the article and avoid bad spots in the vulcanizates.

Tires and Inner Tubes--

The manufacturing of inner tubes involves compounding, extrusion, and curing. These are common operations in rubber products fabrication and have been discussed earlier in this section. This segment of the industry represents only 3% of the value of product shipments in the total tire and inner tube industry. In the following sections, the operations specific to tire manufacturing are discussed.

Tires are built from several parts as illustrated in Figure 8. There are three variations in tire construction: conventional, belted bias, and radial ply tires, as shown in Figure 9. Different rubber compounds are used in making the several tire parts because each part performs a different function. The carcass (made of body fabric or cord plies), the impact plies (which are placed between the body plies and the tread to provide extra

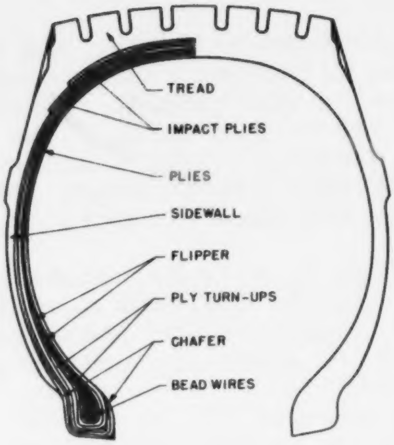

Figure 8. Cross section of a tire (14).

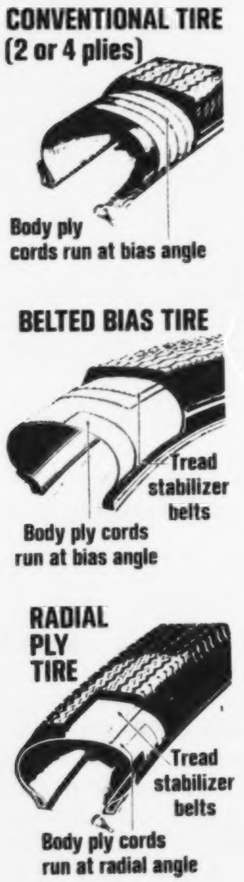

Figure 9. Variations of tire construction (11).

impact resistance), the bead assembly, the tread, and the tire wall are all made from different rubber compounds. Tire manufacturers use both synthetic and natural rubber, the latter mainly for steel belted and large size tires. The basic recipes for rubber compounds are generally very similar except that synthetic compounds require different carbon black loadings, somewhat more softener, less sulfur, and more accelerator.

The basic steps involved in tire manufacturing are schematically shown in Figure 10. Recipes for each specific part of the tire are selected, and the compounds are prepared using roll mills and Banbury mixers. Table 17 lists typical compositions of the rubber compounds for different tire parts. All ingredients except sulfur and the accelerator are added to the rubber in a Banbury mixer. The batch is then dumped on a roll mill, shown previously in Figure 5, located below the mixer for addition of the curing ingredients. Compounded rubber is made into standard sheets which are then used to manufacture the individual tire parts.

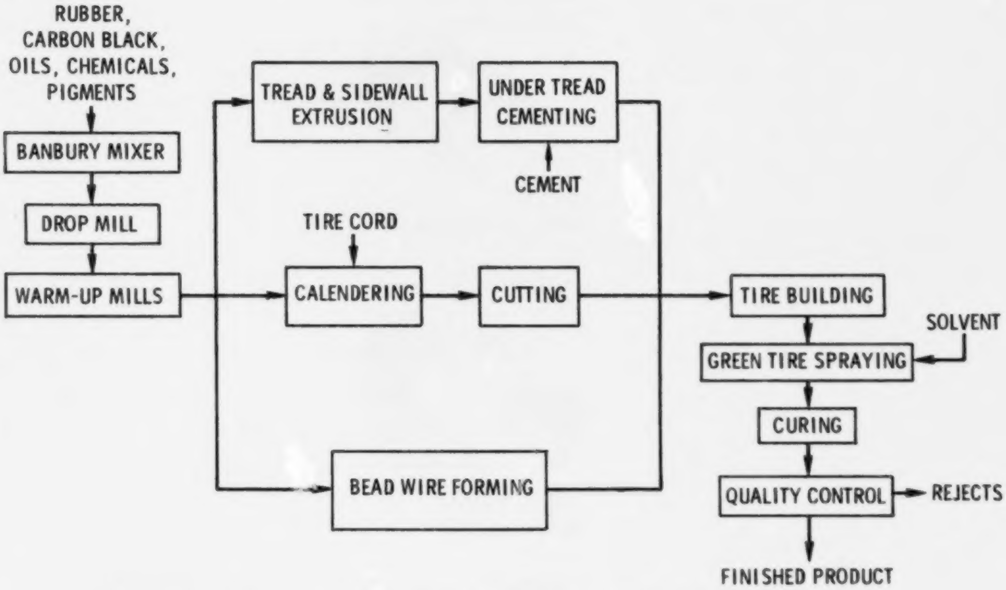

Figure 10. Tire plant process flow diagram.

Carcass plies are made of cord fabric insulated with rubber compounds. A variety of carcass materials are available to the tire manufacturer: cotton, rayon, nylon, polyester, steel wire, and glass fiber. The last two materials are used in radial tires. Today, very little cotton cord is used in pneumatic tires. Cotton has been replaced by rayon and more recently by nylon. The increasing popularity of radial tires has increased the use of steel wire and glass fiber in tire manufacture. Selection of the cord fabric depends primarily on cost because tire cords represent a large portion of the cost of tires.

TABLE 17. TYPICAL COMPOUND COMPOSITIONS FOR TIRE PARTS (14)

Tire part	Component	Parts by weight
Inner carcass or body plies (truck tires)	Natural rubber	100
	SRF black	25
	Zinc oxide	3
	Stearic acid	2
	Softener	5
	Antioxidant	1
	Sulfur	2.8
	Primary accelerator	0.75
	Secondary accelerator	0.15
Outer carcass or body plies (truck tires)	Natural rubber	100
	SRF black	15
	EPC black	20
	Zinc oxide	3
	Stearic acid	2
	Softener	5
	Antioxidant	1
	Sulfur	2.8
	Primary accelerator	0.75
	Secondary accelerator	0.15
Impact plies	Natural rubber	100
	EPC black	40
	Zinc oxide	3
	Stearic acid	2
	Softener	5
	Antioxidant	1
	Sulfur	2.80
	Primary accelerator	0.80
	Secondary accelerator	0.20
Beads	Natural rubber	100
	SRF black	120
	Zinc oxide	8
	Precipitated whiting	15
	Softener	11
	Stearic acid	5
	Sulfur	3
	Accelerator	1.5
Treads	Natural rubber	100
	EPC black	45
	Zinc oxide	3
	Stearic acid	2
	Softener	3
	Antioxidant	1.50
	Sulfur	2.75
	Accelerator	0.90
Inner tubes	Natural rubber smoked sheets	100
	Peptizer	1
	Zinc oxide	4
	Fine thermal carbon black	40
	Antioxidant	2
	Paraffin	1
	Sulfur	1.5
	Primary accelerator	1.4
	Secondary accelerator	0.2

Rubber compound used to manufacture tire plies must adhere to the cord fabric and have enough tack to hold together while the green (unvulcanized) tire is being assembled and cured. Impact plies are built somewhat tougher than inner plies since they must remain intact to divert road shocks and bind the rigid carcass of the tire to the tire tread. Both sides of cord plies for the tire carcass are coated at once on a four-roll calender.

Its relatively rough surface texture allowed natural rubber stocks to be applied directly to cotton cord. This is not feasible with rayon and nylon cords, which must be coated with an adhesive before the cord fabric can be coated with rubber compound in the calender. Medium styrene-butadiene and butadiene-styrene vinyl pyridine latexes are usually used in this application. Vinyl pyridine latexes are universally used for nylon tire cord. A typical tire cord dip solution is given in Table 18.

TABLE 18. TYPICAL TIRE CORD DIP SOLUTION (13)

Material	Dry, parts	Wet, parts
SBR type 2000 latex at 40%	80	200
Vinylpyridine latex at 47%	20	43
Stabilizer (20% Dresinate 731)	1	5
Water to 20% solids		78
Resin solution (6.5%)	17.3	266
TOTAL	118.3	592
Resin solution formula		
Water to 6.5%		238.5
NaOH	0.3	0.3
Resorcinol	11.0	11.0
Formaldehyde (37%)	6.0	16.2
TOTAL	17.3	266

In the normal sequence of operations, ply fabric is passed through the adhesive dip solution, the excess dip is removed, the coated fabric is dried to a moisture level less than 1%, the rubber compound is calendered on both sides of the cord fabric, and rubber cement is applied to the carcass. The last step is necessary only for carcass plies with a high percentage of synthetic rubber compounds because the tack of synthetic rubber is insufficient for it to adhere properly to the vulcanized rubber. Finally, the fabric is cut to a specific angle and the required width on a bias cutting machine.

Wire bead, made of several strands of high carbon steel, is used to keep the tire on the rim. Each strand is coated with rubber compound while passing through an extruder. Several strands are passed simultaneously through the die of the extruder, then rolled together to make the bead. The bead is wrapped with rubberized square woven fabric, then rewrapped with the same fabric, the edges of which extend upward into the sidewall where they can be anchored into the lower sidewall of the tire.

The tread and sidewall of the tire are formed by extrusion through dies. The extruded profile is designed to provide sufficient rubber to fill in the tread and sidewall pattern in the mold.

Tire tread is made of two sections: the cap, which contacts the road; and the base, the section next to the carcass. Since the two sections are made of different rubber compounds, dual extruding units have been developed. Good adhesion between the cap and the base is important, and in dual extrusion, these two parts are plied together hot. Some extruding machines produce the cap and base already joined. Passage through a water bath cools and shrinks the continuous tread slab, which is then cut to the correct length for tire assembly.

Tires are assembled on rotating drums having a diameter slightly larger than that of the tire. Individual tire parts are supplied to the builder in a form that allows the fastest assembly of the tire. Carcass plies are cut to the proper angle, width, and length and may be delivered in rolls that allow unreeling of the fabric without strain (to avoid angle distortion), or in bands of two to four plies. The treads and sidewalls are also delivered precut to length. Synthetic rubber tread is delivered with crude rubber cement on its underside and ends to ensure proper adhesion to the tire carcass.

Four to eight cord plies are applied to the drum without stretching; each is tied under and over the bead in a manner which securely locks the bead. Natural rubber plies usually have enough tackiness to adhere to themselves. Synthetic rubber plies are coated with a rubber cement to provide sufficient tackiness. If impact plies are used, they are added next, followed by the sidewall and tread sections. At this point, the assembled tire is cylindrical in shape.

Usually the whole tire is assembled on the drum by one man, but machines have been developed that automatically rotate the drum through several stations for addition of the successive parts. The drum is then collapsed to release the tire, which gains its final shape during vulcanization in the mold. The inside contour of the tire is formed by a curing bag placed inside the tire. The bag fulfills two functions: it gives the tire the proper shape, and it provides a container into which heat and pressure can be applied to vulcanize the inside of the tire. Heat and pressure are supplied by various combinations of steam, air, and water.

Tire shaping and curing equipment have undergone several developments. The curing bladder is an integral part of a new curing press. This combines the forming and curing operations in a single machine and eliminates the labor of inserting and removing the curing bag. Because the bladder is a part of the press and also is thinner than the separate bags, more effective use of internal heat in curing the tire and a significant reduction in curing time are achieved. Tires are vulcanized at 100°C to 200°C for 20 min to 60 min. Longer times are required to cure large truck tires.

Rubber Footwear--
The process description presented here (4) pertains to the production of canvas footwear, which constitutes the major product type within the Rubber and Plastics Footwear Industry, SIC 3021. Canvas shoes are the product of a number of processing operations. These include compounding of rubber stocks, molding of the soles, cutting and fabricating of canvas parts, extrusion of other rubber components, construction of the final product from all these items, and curing of the final product. A flow schematic is shown in Figure 11.

The various rubber stocks received at a canvas footwear plant are compounded with other processing chemicals in Banbury mixers or roll mills and then sheeted out. The compounded, sheeted stock is next cooled. Water spraying or immersion in a cooling water tank are the preferred techniques. After cooling, the sheeted rubber is dipped in an antitack solution to prevent sticking during storage.

A canvas shoe is built from four major components: soles, inner soles, canvas uppers, and boxing. Each of these pieces is made separately by different processes before being brought together in the shoe-building operation.

The soles are either cut from uncured rubber sheets or, more generally, formed using injection, compression, or transfer molding techniques. The technology employed depends on the final product. Compression molding is now more common but requires more manual labor and produces more molding waste than automated injection techniques. The molded soles are deflashed, usually in a buffing machine. A coat of latex adhesive is applied to the soles before they are dried in an oven, which may be electric.

Production of the inner soles begins with the preparation of flat, cellular rubber sheets by extruding or calendering a special rubber stock. The extruded sheet can be continuously cured by passing through heated presses. Blowing agents, such as

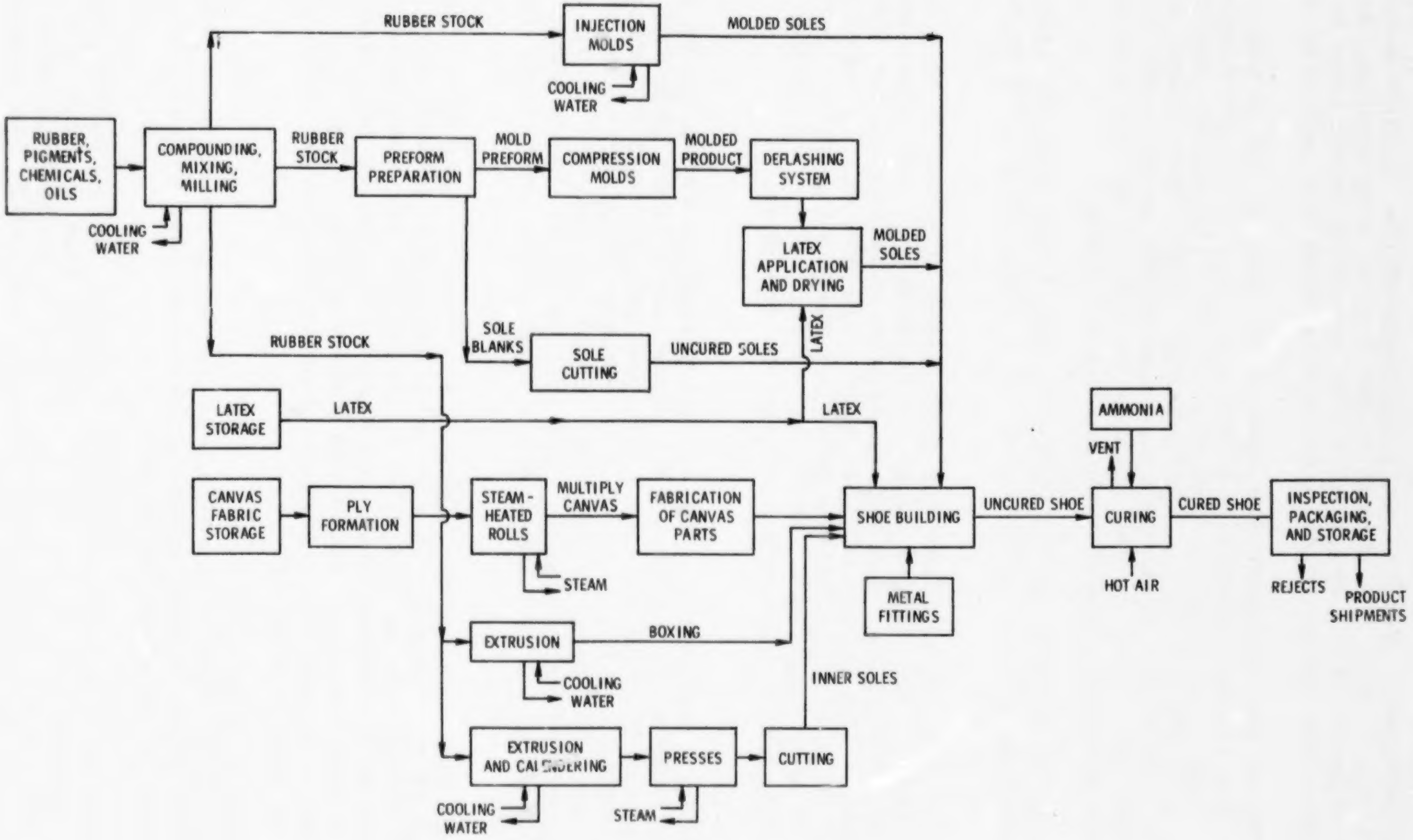

Figure 11. Schematic flow diagram for the production of typical canvas footwear items (4).

sodium bicarbonate ($NaHCO_3$) or azodicarbonamide ($H_2NCON=N-CONH_2$), which are mixed into the rubber stock during compounding, decompose and release gases which blow the extruded sheet into cellular sponge. The inner soles are die-cut from the cellular sheet.

Canvas uppers for footwear are made from two- or three-ply fabric. The canvas material is received at a plant as single sheets. These individual plies are coated with latex, pulled together, and passed over a steam-heated drum. The sheets are stacked and then cut to the proper dimensions using a die and a press. The different canvas components making up the footwear uppers are stitched together on sewing machines.

The boxing, or edging, which protects the joint between the sole and the canvas uppers, is extruded as a long strip from rubber stock.

The shoe is fabricated from its four basic components on a form called a last. The canvas upper is cemented at its edges and placed over the last. The inner sole is attached to the bottom of the last. The bottom of the inner sole and canvas combination is dipped in a latex-adhesive solution which will serve to hold the entire shoe together. Next, the outer sole, the boxing, and the toe and heel pieces are attached to the shoe.

The finished shoes are inspected and placed on racks in an air-heated autoclave for curing. Anhydrous ammonia is injected into the autoclave to complete the cure, the amount required ranging from 0.9 kg to 2.3 kg of ammonia for every thousand pairs of shoes cured. The purpose of using anhydrous ammonia is to reduce the tackiness of the product. The curing cycle lasts about 1 hr, at the end of which the ammonia-air mixture is vented to the atmosphere.

Some shoes are cured without ammonia. This is done when the tackiness of the product is not very important or when the compounding recipe can be modified to eliminate the tackiness often associated with conventional air curing. Steam is not used for curing because it would stain the canvas parts of the shoe in many cases. In addition, curing is not necessary in some new methods of shoe production.

Rubber Hose and Belting--

Rubber Belting--Operations involved in the production of rubber belting are compounding, forming, building, and curing (4). A flow schematic is shown in Figure 12.

Compounding and mixing are usually carried out in Banbury mixers, although compounding mills may be used in some facilities. After mixing, the rubber stock is sheeted out on a sheeting mill and dipped in a soapstone slurry to reduce its tack. The rubber

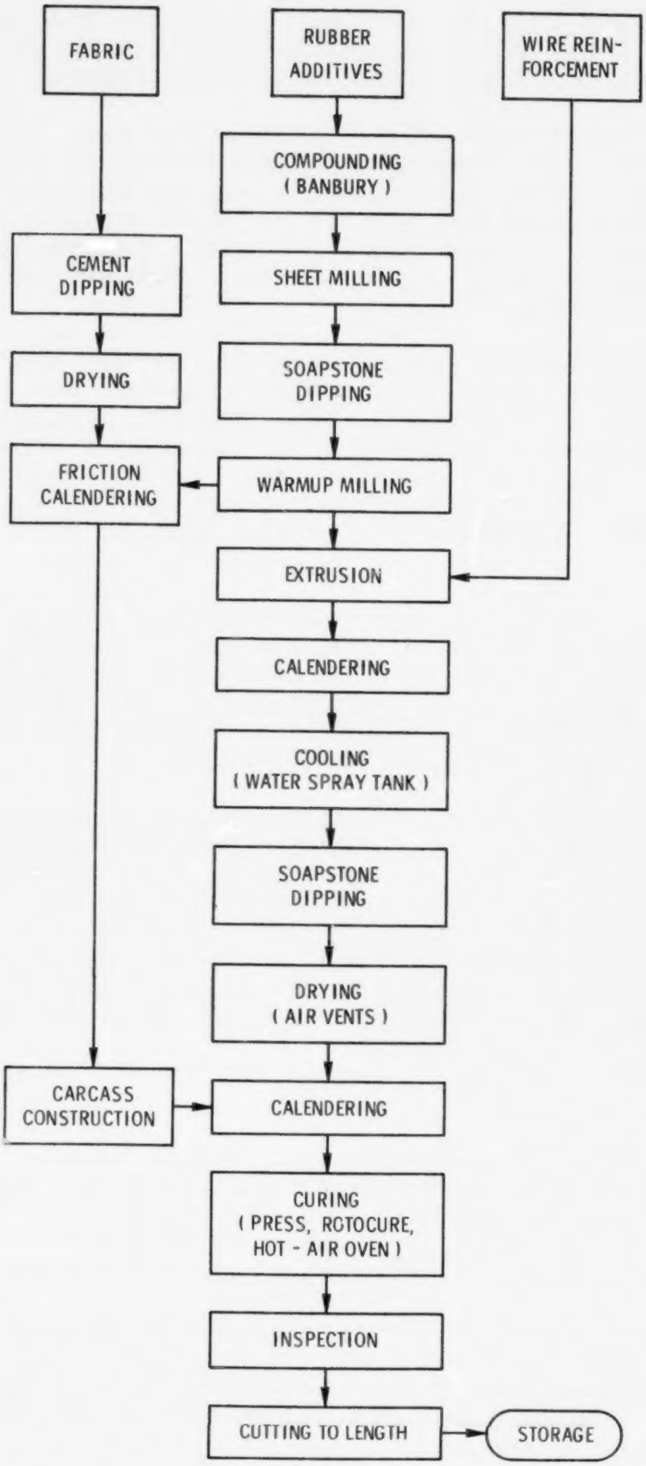

Figure 12. Belting flowsheet.

leaves the rolling mill in a ribbon up to 2 m wide and approximately 25 mm thick. Both the frictioning and sheeting stocks are worked on warmup mills prior to subsequent forming operations.

In the forming operations, the hot sheeting stock passes from the warmup mill through an extruder-calender machine where its dimensions are fixed. Wire reinforcement may be extruded with the rubber stock during this operation to increase the strength of the belting. After calendering, the sheet rubber is cooled in a water spray tank, dried via passage over hot air vents, and rolled up for storage.

The frictioning compound passes from the warmup mill to a friction calender where it is impregnated into the fabric used to build the carcass of the belt. This fabric, usually rayon or nylon, is pretreated by dipping in latex and/or cement and drying to a moisture content of less than 1%. Drying is carried out immediately prior to frictioning by passing the dipped fabric over steam-heated cylinders or platens kept at 115°C or in other types of ovens.

In the building operation, the rubberized, single-ply fabric leaving the calender is used to build belt carcasses of multiple-ply thickness. A variety of techniques are employed in this operation, depending on the specifications of the final product. Once built, the carcass is sandwiched between two layers of rubber sheeting by a calendering operation.

Belt vulcanization (curing) is performed in presses, rotocures, or hot-air curing ovens. A rotocure employs a combination of steam, cooling water, and electric heaters to continuously vulcanize the belting as it passes around the curing drum. Press curing is effected by two heated belts which hold the belting between them under pressure, turn, and drag the belting through the press. Unlike the rotocure, the press-curing technique is a batch operation. Vulcanization requires about 30 min at 140°C.

After curing, the belting is inspected, cut to length, and stored before shipment.

Rubber Hose--There are four types of rubber hoses: machine-wrapped ply hose, hand-built hose, braided hose, and spiralled hose. Similar operations are involved in the manufacture of these four types of hoses. The process description presented here is specific to the production of machine-wrapped ply hose.

Machine-wrapped ply hose consists of three components: the tube (lining), the reinforcement, and the outer cover. The reinforcement is constructed from rubber-impregnated fabric, while the tube and cover are made entirely from rubber. A schematic flow diagram is shown in Figure 13.

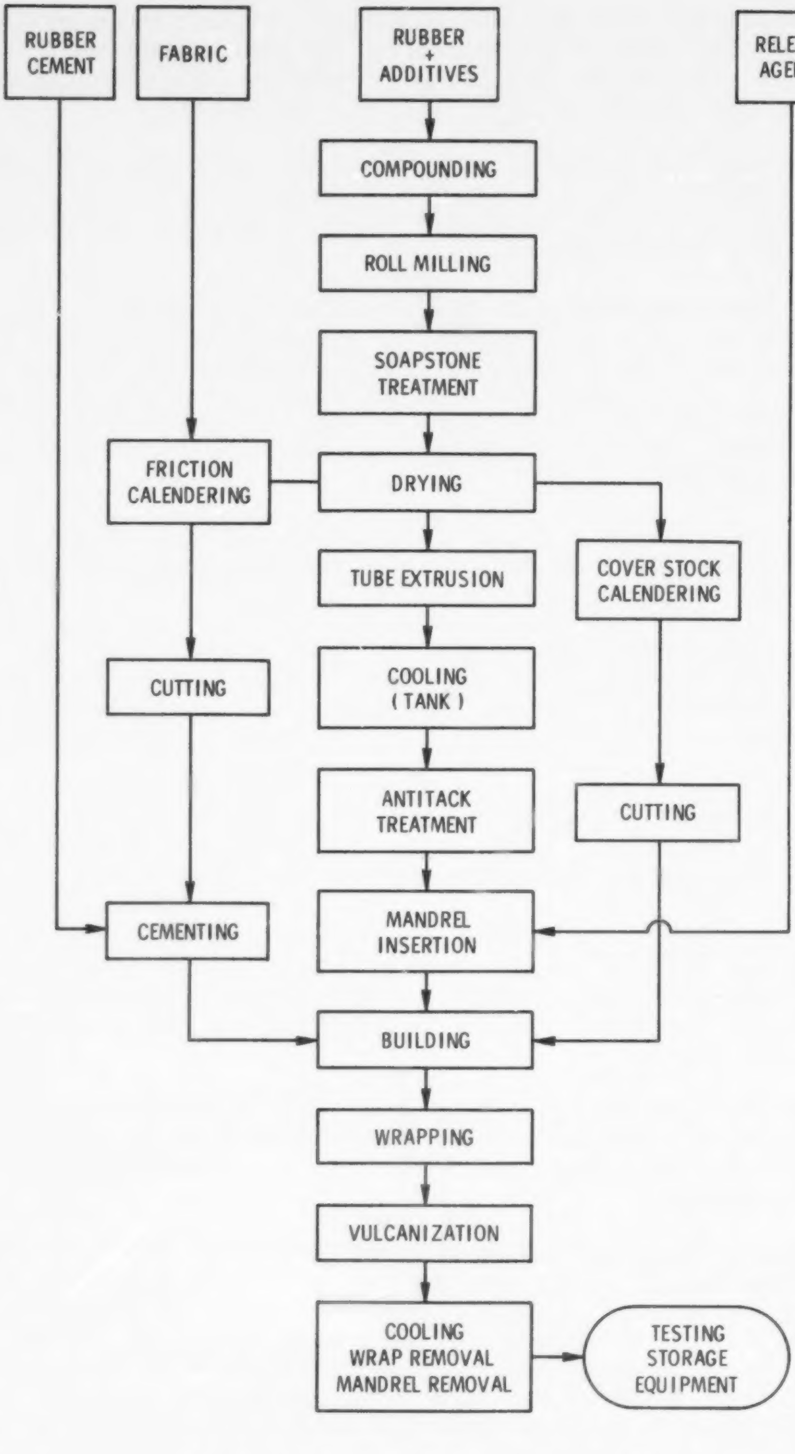

Figure 13. Ply hose flowsheet.

Tube is formed by continuous extrusion. Reinforcement is made by impregnating the fabric with rubber on both sides by friction calendering. The other cover is formed by calendering a thin sheet of rubber stock to the required thickness.

The formed tube is taken to the building area where it is temporarily enlarged via air pressure and mounted on a rigid mandrel. Lubricants are injected into the tube to prevent it from sticking to itself or to the mandrel.

The actual hose building is carried out on a special purpose "making machine" which consists of three long steel rolls. Two of the rolls are fixed parallel to each other in the same horizontal plane, while the top roll is mounted on lever arms so it can be raised and lowered. One or more of the rolls are power driven. Rubber cement is applied to the reinforcement before the building operation.

The green hose is cured in an open steam autoclave at some predetermined temperature and pressure. The necessary pressure is maintained by cotton or nylon wraps.

When vulcanization is complete, the autoclave is vented, the hose is removed and cooled, and the cloth wrap is stripped away. The hose is then removed from the mandrel with compressed air or water and hydraulically tested before final storage and shipment.

Fabricated Rubber Goods N.E.C.--
This industry can be separated into general molded products, general extruded products, and rubber goods from latex. The process description for these rubber products is given below.

General Molded Products--This category includes items such as battery parts, rubber rolls, rubber heels and soles, water bottles, fountain syringes, nipples, pacifiers, rubber bands, finger cots, erasers, brushes, combs, mouth pieces, and a wide variety of mechanical goods.

Rubber molding typically consists of the following operations: 1) compounding of rubber stock, 2) preparation of the mold preforms or blanks (milling, calendering, and cutting), 3) molding, and 4) deflashing.

Metal-bonded items, which consist of a molded rubber component bonded to the metal part, are manufactured in a manner similar to that for other molded rubber products. Additional operations are metal degreasing and subsequent adhesive spraying on the metal surface to provide good adhesion between metal and rubber. Various molding techniques have been mentioned earlier in this section. Vulcanization is accomplished in the molding operation.

General Extruded Products--General extruded products include rods, tubes, strips, channels, mats and matting, floor and wall covering, and stair treads. Operations involved are compounding, milling, calendering, extrusion, curing, and bonding of extruded parts.

In the curing operation, rubber articles that would sag or flatten under their own weight before they could completely set up must be supported. In most cases, such articles are embedded in talc or powdered soapstone. However, rubber tubing is placed on a mandrel and wrapped with fabric to insure proper curing. Vulcanization usually requires about 30 min at 140°C to 150°C (4).

In the bonding of extruded and cured rubber parts, two or more parts to be connected are inserted into a mold where uncured rubber material is applied to the joint and is vulcanized in the press. Solvent is used for lubrication in the insertion of rubber parts and for tackifying rubber parts.

Fabrication of Rubber Goods from Latex--The first requirement in production of rubber articles from latex is to bring the rubber latex and all the compounding ingredients into solution or dispersion form. Solution is used when all of the ingredients are water soluble. Frequently, the ingredients are not water soluble, and it is necessary to emulsify the liquid ingredients and disperse the solid materials in water.

Dispersions are generally prepared from a coarse slurry of powder with water containing small amounts of dispersing agents and stabilizer. The slurry is then ground on a suitable mill to give the desired particle size. The function of the dispersing agent is to keep the particles suspended. Typical dispersing agents are sodium 2-naphthylene sulfonate and formaldehyde, and an alkyl metal salt of sulfonated lignin. The amounts of dispersing agents must be determined experimentally. A wetting agent is usually used, in concentrations less than 1% by weight, to produce a satisfactory dispersion.

Dispersions are prepared using grinding equipment such as colloid mills which break aggregates but do not change the particle size. Colloid mills are used for clay, precipitated whiting, zinc oxide, etc. Grinding equipment that reduces ultimate size and breaks agglomerates is used for solids such as sulfur, antioxidants, and accelerators. Ball and pebble mills, ultrasonic mills, and attrition mills are used for this purpose. Typical recipes and directions for preparing dispersions of antioxidants such as Aminox and of ultraaccelerators such as zinc dimethyldithiocarbonate (Methazate) are given in Tables 19 and 20.

TABLE 19. PREPARATION OF A DISPERSION OF AMINOX SUITABLE FOR LATEX COMPOUNDING (13)

Material	Weight	Procedure
A. Water	68	Add A to ball mill
B. Water	22.8	Make up B separately and add to mill
Ammonia (28% NH_3)	1	Add C and D to mill
Blancol[a]	4	Ball mill 4 days--keep cooling water on to avoid sintering Aminox
Dowicide A[b]	0.2	
Casein	2	
C. KWK bentonite	2	
D. Aminox	100	
TOTAL[c]	200	

[a] Trademark of GAF Corporation.

[b] Trademark of Dow Chemical Company.

[c] Total solids, 54.2%; active solids, 50%.

TABLE 20. PREPARATION OF A DISPERSION OF METHAZATE SUITABLE FOR LATEX COMPOUNDING (13)

Material	Parts by weight	Procedure
A. Water	70	Add A to ball mill
B. Ammonia (28% NH_3)	1	Make up B and add to ball mill
Blancol	4	Add C to ball mill
Dowicide A	2	Ball mill 48 hr
Casein	2	
Water	22.8	
C. Methazate	100	
TOTAL[a]	200	

[a] Total solids, 53%; active solids, 50%.

Emulsions are prepared by first making a coarse suspension of liquid ingredient droplets in water and then exposing this mixture to an intense shearing in a colloid or ultrasonic mill or a homogenizer (a machine that forces the emulsion through a fine orifice under high pressure). Emulsions can also be simply prepared by adding the material to a soap solution. Soap can be prepared quickly in the machine by adding fatty acid or anionic parts such as a stearic, oleic, or rosin acid to a solution of potassium hydroxide or an amine in water. Examples of emulsion recipes are presented in Tables 21 and 22.

TABLE 21. PREPARATION OF A NAUGAWHITE EMULSION SUITABLE FOR LATEX COMPOUNDING (13)

Material	Dry parts	Wet parts	Procedure
Water (hot)		19	Add Nopco 1444B[a] to hot water with high-speed stirring.
Nopco 1444B	5.4	6.0	
Naugawhite	75	75	Add Naugawhite slowly, allowing a few minutes between additions.
TOTAL	80.4	100	After all the Naugawhite has been stirred in, continue stirring for 15 min.

[a] Nopco 1444B is a highly sulfonated castor oil produced by Nopco Chemical Company.

TABLE 22. PREPARATION OF AN OIL EMULSION SUITABLE FOR LATEX COMPOUNDING (13)

Material	Parts	Procedure
A. Mineral oil	70	Add A to B using an agitator such as the Eppenbach Homo-mixer.
Oleic acid	1.5	
B. Potassium hydroxide	1.5	Put emulsion through a homogenizer to obtain a very small particle size and a high emulsion stability.
Water	27	
TOTAL	100	

The preparation of the latex compound is a very simple operation. It consists of weighing and mixing the proper amounts of various solutions, emulsions, and dispersions. This is done in a large tank with a mechanical agitator.

Rubber articles can be fabricated using compounded latex by a variety of methods. One of the simplest techniques is to dip a form into the latex and dry the thin film formed on the form at room temperature or in warm air at 49°C to 60°C while rotating the form to ensure a uniform film thickness. Thicker films are made by multiple dipping.

Another technique for fabricating rubber articles uses porous forms, or porous molds, made of plaster of paris or unglazed porcelain with smaller pore size than the smallest rubber latex particles. The rubber particles are filtered out by this material and latex coagulates to form a film due to the presence of calcium ions in the plaster. The molds are dried in an oven at

60°C for one hour. This can be repeated for 30 min after the articles are removed from the mold. For example, dolls and squeeze toys are manufactured using this technique.

Since the rubber particles in latex are negatively charged, electrodeposition has been used to coagulate rubber and make rubber articles. However, evolution of oxygen on the anode produced oxidation of the product and caused porosity in the article. Electrodeposition was therefore abandoned. Essentially the same degree of coagulation can be attained by using chemical coagulants.

A thin layer of a chemical coagulant is produced by dipping the form in the coagulant solution and evaporating the solvent, preferably alcohol. The thin layer of coagulant can be produced either directly on a clean form or on a form that is coated with a very thin layer of the latex. The form is then dipped in the latex. When the film attains the desired thickness, it is washed in hot water at 60°C to 71°C for about an hour to remove the coagulant and all other water-soluble ingredients. The film is then dried in air at room temperature, and the article is cured in a 66°C oven.

Typical coagulants are calcium chloride or calcium nitrate in a solution of denatured ethyl alcohol. They are mixed with a nonionic surfactant and a release agent (a fine, insoluble powder such as talc, clay, or diatomaceous earth) which is suspended in the coagulant. The surfactant and release agent are used to aid in wetting the form and releasing the article from the form, respectively.

Another variety of this process uses a gelling agent (electrolyte with a weak coagulating effect such as ammonium salts and sodium fluorosilicate) in metal molds. This method offers the advantage that latex sets to the gel with no change in volume and without distortion.

Some rubber products may be made by extrusion of the latex. For example, latex thread is produced by extrusion of the latex compound through fine orifices into a coagulant bath which gels the thread. The thread is then toughened, washed, dried, and cured. Dilute acetic acid is usually used as the coagulant bath.

The broadest application for both latexes, natural and synthetic, is foam sponge. There are two basic processes available, the Dunlop and the Talalay process, applied in different variations. In the Dunlop process, which is the most commonly used, the latex is whipped to a froth by the mechanical incorporation of air into the latex. The Talalay process produces the froth by chemical rather than mechanical means. Hydrogen peroxide and an enzymic decomposition catalyst are used for this purpose. Oxygen produced by the decomposition of the peroxide foams the latex mix.

The foam is chilled and CO_2 is introduced to gel the latex. Further treatment is the same as in the Dunlop process.

The frothed structure must be set using a coagulant or a gelling agent. Sodium silicofluoride (Na_2SiF_6) is widely used in this application. Zinc oxide is also believed to take an active part in the process. Sodium silicofluoride decomposes and forms sodium fluoride (NaF), silicon tetrahydroxide [$Si(OH)_4$], and hydrofluoric acid (HF). Zinc apparently reacts with the fatty acid latex stabilizers forming a soluble soap. This destabilizes the latex particles, causing them to coalesce and form a gel. The $Si(OH)_4$ may also form very fine particles which could adsorb stabilizer and further enhance gelation. In very stable latexes, some secondary gelling agents may be utilized to induce gelation. Cationic soaps, other salts, and amines are used for this purpose.

Whipping can be done either continuously or in a batch process. After the gelling agents are added, the foam is poured into molds and cured. Additional curing is done after the product is removed from the mold.

Ammonium acetate or ammonium sulfate, in combination with zinc oxide, are employed as the gelling agents in the production of foam backings for various fabrics such as carpets, scatter mats, and upholstery fabrics. Ammonium hydroxide is the product of the reaction. Once gelation occurs, the foam is spread directly on the fabric or it is spread on a belt and transferred wet to the fabric. The gelling is carried out at elevated temperatures, usually by means of infrared lamps.

Gaskets, Packing, and Sealing Devices--

The principal method of manufacturing rubber gaskets, packing, and sealing devices is molding. Operations involved are the same as those for general molded products in the Fabricated Rubber Goods N.E.C., which is covered in the preceding subsection. The three common molding techniques (compression, transfer, and injection molding) are described later in this section for common operations in manufacturing of rubber products.

Rubber Wire-Insulating (4)--

Extrusion is the preferred method of applying a rubber compound to wire or cable as an insulating and/or protective covering. When a suitably modified extruder is used, plastics as well as rubber may be employed as insulation.

A wire to be covered is passed through a right-angle or side-delivery head. In this operation, the wire is fed through the head in a direction perpendicular to the axis of the extruder screw. The head is designed so that the rubber compound is deflected 1.57 rad (90°) and completely surrounds the wire.

The covered cable is pulled through the machine by a variable-speed hauloff. A satisfactorily uniform coating is ensured by regulation of the drawing speed.

Insulated wire is continuously vulcanized by extrusion directly into a suitable curing device. This is usually just a tube fixed to the nozzle of the extruder and filled with steam at pressures from 1.38 MPa to 1.72 MPa. Such tubes may be 30.5 m to 61 m in length. Residence time for the insulated wire is approximately 15 s. Glands through which the cable exits the tube prevent leakage of steam. Large cables are usually processed in vertical units, but horizontal or catenary-shaped tubes are also available.

The exterior of insulated wire or cable must be protected against mechanical and sometimes chemical deterioration. The type of protective covering applied will depend on the ultimate end use of the cable. Small wires are covered with a braid, normally of cotton but sometimes of rayon or fine metallic wire. Another means of protection, tough rubber sheathing (TRS), can be applied to the insulated wire using an extruder with a side-delivery head as described previously. The sheathing may consist of neoprene (polychloroprene) or another oil-resistant rubber. Lastly, some insulated wires and cables may be covered by an extruded lead sheath applied earlier as a means of support during vulcanization.

Tire Retreading (4)--
The tire retreading process consists of a series of eight unit operations through which worn tires are rendered servicable and fit for resale. With the exception of studded snow tires, nearly every tire size and design is utilized by the industry. The majority of retreaders receive their tires from scrap dealers, but turn-ins are also a popular source of supply.

Raw camelback is nearly always purchased from an outside supplier. Very few retreaders compound their own stock. A schematic flow diagram for tire retreading is presented in Figure 14.

On arrival, the tires are first inspected to determine whether or not the casing and carcass are in good condition. There should be no cuts or visible deterioration of the reinforcing fabric. Hidden ply separations, the major cause of tire failure, are detected by injecting air into the tire shoulders. Since trapped air itself may cause ply separation, the tire is vented in the bead area so the air can escape during molding or on highway flexing. Tires unfit for retreading are usually passed on to the reclaiming industry.

After sorting, the tires are sent to the buffing area where the remaining tread is ground off with a grinding wheel. The surface of each newly buffed tire is rendered dust free with a stiff wire brush.

The clean tire is measured in order to select the correct curing rim and to assure a tight fit in the matrix. Tires can grow up to 7% of their original width from road use, so both the width and wall thickness must be measured. Once measured, the tires are taken to the spray area where they are coated with vulcanizable rubber cement.

After the surface of the tire is coated with cement, strips of tread rubber are wound circumferentially around it and cut to length. Some retreaders "program" the tread on. In this operation, the machinist selects a profile to build, and the machine automatically wraps the thin strand of tread until the exact contour is obtained. The tread-winding process typically requires about 4.53 kg of camelback per passenger-car tire and 15.85 kg per truck tire.

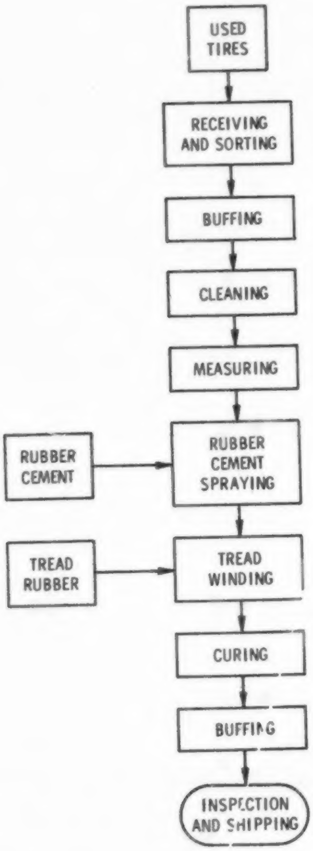

Figure 14. Retreading flowsheet (4).

After tread winding, the tire goes into a mold for curing at some specified temperature for some predetermined length of time. Most curing molds are steam heated, but some older ones are electrical. After curing, the rubber flash is buffed off, and the finished product is inspected and shipped.

GEOGRAPHICAL DISTRIBUTION

Rubber processing plants are distributed among 43 states in the United States (4, 15). Table 23 gives the number of plants in each of these states for industries in the nine SIC's.[a] Also given in this table are percentages by state of U.S. total number of plants, the population density in each state, and the composite state population density. The composite state population density, $\overline{D}$, was calculated by the following formula:

$$\overline{D} = \sum_{i=1}^{43} D_i \cdot \frac{P_i}{100} \qquad (1)$$

where D_i = population density in the ith state

P_i = state percentage of U.S. total number of plants for ith state

Two states, Ohio and California, contain about 25% of the 1,687 rubber processing plants in the United States. Roughly another 25% of the plants are located in Illinois, New York, New Jersey, and Massachusetts. The remaining 50% of the plants are distributed among the remaining 37 states. Figure 15 is a graphic representation of the total number of plants on a state-by-state basis.

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[a] For the tire retreading industry (SIC 7534), only a partial listing is given due to unavailability of complete data.

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(15) 1972 Census of Manufacturers, Volume II: Industry Series, Part 2: SIC Major Groups 27-34. U.S. Department of Commerce, Washington, D.C., August 1976.

TABLE 23. GEOGRAPHICAL DISTRIBUTION OF RUBBER PROCESSING PLANTS (4, 15)

State	Number of plants in each SIC									State totals	Percent of U.S. total	Population density, persons/km^2
	2822	3011	3021	3031	3041	3069	3293	3357	7534			
Alabama		10				11	3			24	1.4	26
Arizona		2				7				9	0.5	5
Arkansas		5	1		1	6				13	0.8	14
California	2	22	4		7	144	29	2		210	12.5	49
Colorado		3			1	3	2			9	0.5	8
Connecticut	1	1	1	2	1	46	6	2		60	3.6	240
Delaware	1	1			3	2				7	0.4	107
Florida		2	2			22	1			27	1.6	49
Georgia	2	9	2			31		1		45	2.7	31
Illinois	1	10	1	1	5	61	22	1		102	6.0	77
Indiana		5	2		2	56	5	1	1	72	4.3	56
Iowa		5				5				10	0.6	20
Kansas		2								2	0.1	11
Kentucky	2	3				4	1	1		11	0.6	31
Louisiana	3									3	0.2	81
Maine		1	3							4	0.2	12
Maryland		2	2			10	2			16	1.0	153
Massachusetts	2	6	6		3	64	9	2		92	5.5	280
Michigan	1	6			2	57	12		1	79	4.7	60
Minnesota		1			1	24	4			30	1.8	19
Mississippi		3		1		11				15	0.9	18
Missouri		4	2		1	13	5			25	1.5	26
Nebraska						5				5	0.3	7
Nevada					2					2	0.1	2
New Hampshire		3	4			2	1			10	0.6	32
New Jersey		3	2		12	70	11	1		99	5.9	369
New York		4	5	1	4	68	17	2		101	6.0	147
North Carolina	2	7	2		1	18	3	1	1	35	2.0	40
Ohio	2	27	3	1	10	174	18	2	1	238	14.1	100
Oklahoma		7				7	3			17	1.0	14
Oregon		3				11				14	0.8	8
Pennsylvania	2	14	5		3	49	12	1	1	87	5.2	101
Rhode Island						16				16	1.0	366
South Carolina		2			1	9				12	0.7	33
South Dakota						1				1	[a]	3
Tennessee	2	13	3		1	13	2			34	2.0	37
Texas	6	11				40	16			73	4.3	17
Utah					1	5	2			8	0.5	5
Vermont						1				1	[a]	18
Virginia		5				13	1			19	1.1	45
Washington		2				5				7	0.4	20
West Virginia			1			8	2			11	0.6	28
Wisconsin		2	1			24	5			32	1.9	31
TOTAL	29	206	52	6	62	1,116	194	17	5[b]	1,687	99.9	103

[a] Less than 0.1%.

[b] This includes the tire retreading shops that have been identified and represents only a portion of the plants in SIC 7534.

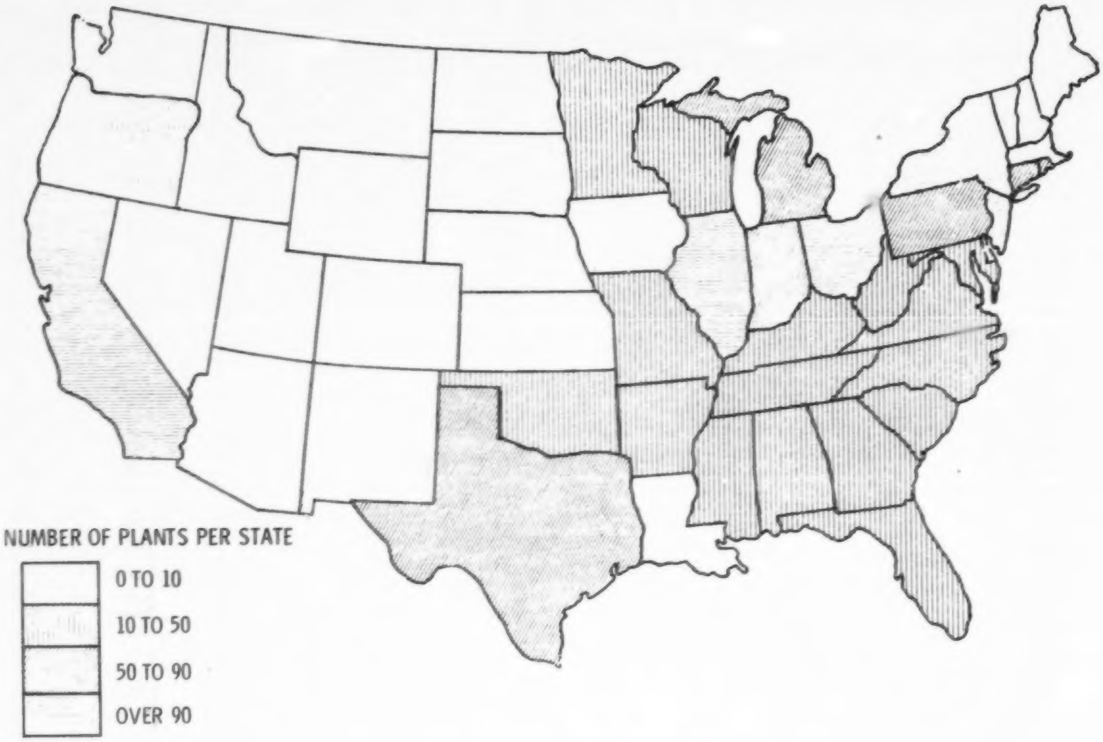

Figure 15. Geographic distribution of rubber processing plants in the United States.

SECTION 4

EMISSIONS

LOCATIONS AND SELECTED POLLUTANTS

Emissions from rubber processing plants are a function of the unit operations performed and the chemical substances used during processing. The materials emitted include particulates (carbon black, zinc oxide, soapstone, oil mists, etc.) and hydrocarbons (monomers, volatilized rubber chemicals, rubber impurities, solvents, etc.). The locations of these emissions and the specific pollutants selected for assessment of environmental impact are given below for each industry.

SBR Production

Emulsion Polymerization--

Emission points for the emulsion polymerization process are 1) the tank farm or monomer storage area, 2) the polymerization or reactor section, 3) the recovery area, 4) the carbon black operation, and 5) the finishing area.

The tank farm emissions result from breathing losses in styrene storage. Butadiene is stored in pressurized vessels, sometimes located underground or underwater, and thus would not be expected to have breathing losses. Fugitive losses due to leaks in pump seals and valves also exist in the tank farm area, as do losses from the storage of other liquid organics or solvents such as reactor coolant and gasoline.

Polymerization or reactor section emissions result from fugitive losses, due again to pump seal and valve leaks. The specific substances emitted have not been identified and quantified. However, total hydrocarbon emissions have been reported and are considered in this report (4). As the reactor itself is pressurized, no emissions would be expected from it.

Hydrocarbon emissions from the recovery area are also due to fugitive losses from compressor seals, pump seals, and pipeline valves and seals (4). In addition, emissions of unrecovered butadiene occur after adsorption, absorption, or condensation (4).

More than two-thirds of all SBR crumb are "extended" by addition of oil and/or carbon black. The addition of carbon black prior to coagulation results in emissions of carbon black particles (16). Emissions from the finishing area in crumb rubber production result from drying and baling operations. During the drying operation unreacted and unrecovered styrene is emitted. Also, fine particles of SBR are contained in the exhaust gas from the dryer. In the baling operation, talc is applied to the exterior of the bale to prevent the rubber from sticking to polyethylene film used to wrap the bale. The dusting is accomplished by air-blowing the talc onto the bales as they pass through a "dust chamber" on a conveyor belt. This is a source of particulates (talc) emissions. When latex rubber is produced, the above emissions do not exist.

Solution Polymerization--

Emission points for the solution polymerization process are 1) the tank farm area, 2) the reactor area, 3) the carbon black application, 4) the desolvent area, 5) the monomer and solvent purification area, and 6) the finishing area.

Emissions from tank farm area, reactor area, and carbon black application are similar to those mentioned for emulsion polymerization. The only difference is the additional hydrocarbon emission from solvent storage (usually hexane). The desolvent area has emissions primarily of hexane resulting from the slurried crumb being transferred to the finishing area. The slurry is held in surge tanks, which are vented to the atmosphere. In addition, fugitive losses in this area and in the solvent and monomer purification area due to pump seal and valve leaks are present (4). Emissions from the drying operation in the finishing area are almost entirely hexane (solvent which is held tightly within the crumb even after steam stripping and dewatering) (4). The particulate emissions from talc dusting in baling operations are similar to those of the emulsion polymerization process.

Rubber Reclaiming

The depolymerization operation is the primary emission point of hydrocarbons in rubber reclaiming. The pan, mechanical, or digestion processes emit vapors and mists resulting from the addition of aliphatic and aromatic oils and solvents during digestion or reclaiming. In addition, rubber particles are emitted from size reduction of scrap rubber before charging into the depolymerization equipment. In the baling operation, talc is applied to the reclaimed rubber to prevent sticking. As in the baling operation in crumb SBR production, this is a source of particulate emissions.

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(16) Pervier, J. W., R. C. Barley, D. E. Field, B. M. Friedman, R. B. Morris, and W. A. Schwartz. Survey Reports on Atmospheric Emission from the Petrochemical Industry, Volume 4: Styrene Butadiene Rubber via Emulsion Polymerization. EPA-450/3-73-006d, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, June 1974. 39 pp.

Tires and Inner Tubes

Emission sources in tire manufacturing include 1) compounding, 2) milling and calendering, 3) fabric cementing, 4) extrusion, 5) undertread cementing, 6) green tire spraying, and 7) curing.

Emissions from compounding consist of particulates and hydrocarbons. The particulates are solids (carbon black, zinc oxide, soapstone, etc.) and liquid aerosols (organic additives) (17). The hydrocarbon vapors originate from impurities in the rubber and from the organic additives. They occur as a result of heat generated during mechanical mixing of the batch. Particulate emissions occur when the additives are introduced into the batch. In general, these particles are in a finely divided form and smaller than 15 μm (16).

Compounding units are equipped with exhaust hoods that remove the heat generated by the mixing action. They also remove particulate and hydrocarbon emissions from the work area. Bag filters are employed to recover the solid particulates for recycle within the plant (17).

During the milling and calendering operations, heat is also generated from the mechanical working of the rubber. Hydrocarbon vapors are therefore present and emitted to the atmosphere. For the same reason, extrusion is another source of hydrocarbon emissions. In most cases the operating temperature in the extrusion operation is relatively low (below 50°C), resulting in a smaller quantity of hydrocarbons emitted. Hydrocarbons from milling, calendering, and extrusion operations are usually emitted to the general work area and vented through the plant ventilation system (4).

In the fabric cementing operation, ply fabric is cemented or latex-dipped and dried before calendering of the rubber and fabric. Large quantities of solvent hydrocarbons are emitted particularly in the drying step of the operation. In undertread cementing, solvent-based cement is used to tackify the tread before it is sent to the tire building operation. Generally, naphtha-based solvents are used, and they evaporate rapidly after being applied.

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(17) Air Pollution Engineering Manual, Second Edition. J. A. Danielson, ed. Publication No. AP-40, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, May 1973. 987 pp.

Green tire spraying, which is one of the building operations, utilizes two distinct solvent-based sprays (one internally and one externally) to act as mold release agents and rubber flow promoters during the curing operation (18). The solvents used in this operation evaporate both inside and outside of the spray booth used.

In the curing operation, vulcanization temperatures (100°C to 200°C) result in the emission of organic materials from the rubber stock. Theoretically, these emissions can occur via two distinct mechanisms: 1) the volatilization of species present in the stock and 2) the formation of new compounds.

The available literature indicates that emissions occur primarily among ingredients which are either liquids at room temperature or solids with melting points at or below curing temperatures. On this basis, the possible species emitted can be determined as indicated below (19).

Polymer or Blend Volatiles--General purpose polymers do not decompose until pyrolysis temperatures (300°C to 400°C) are reached. Depolymerization reactions have been noted only upon continued heating at 175°C to 225°C for several hours. Curing operations of much shorter duration result in little or no breakdown. Hence, polymer emissions will be the result of residual monomer and impurities from the manufacturing process and should represent less than 1% of the total polymer by weight.

Monomers however, are sufficiently volatile that appreciable amounts may be lost in precuring operations such as milling and calendering. Typical boiling points are 145°C for styrene, 78°C for acrylonitrile, and 54.9°C for chloroprene.

Antioxidants and Antiozonants--In most cases, emissions of phenolic compounds are higher than those of amines. Total emissions are greater in black stocks than in gum. The total emissions from curing molds may range as high as 5% to 20% for thin stocks and the more volatile antidegradants. However, normal vaporization losses amount to only 0.5% to 1.0% by weight of the antidegradant present in the stock. The melting points of the common antioxidants are given in Table 24.

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(18) Van Lierop, G., and P. W. Kalika. Measurement of Hydrocarbon Emissions and Process Ventilation Requirements at a Tire Plant. Presented at the 68th Annual Meeting of the Air Pollution Control Association, Boston, Massachusetts, June 15-20, 1975. 23 pp.

(19) Rappaport, S. M. The Identification of Effluents from Rubber Vulcanization. Ph.D. Thesis, University of North Carolina, Chapel Hill, North Carolina, 1974.

TABLE 24. MELTING POINTS OF COMMON ANTIOXIDANTS (19)

Antioxidant type	Compound	Melting point, °C
Phenol	2,6-Di-*t*-butyl-4-methylphenol	69 to 70
	2,4-Di-*t*-amylphenol	Liquid
	3-*t*-Butyl-4-hydroxyanisole	Liquid
	2,2'-Methylene-bis(4-methyl-6-*t*-butyl phenol)	125 to 130
Amine	Phenyl-β-naphthylamine	105 to 106
	N-*N*'-diphenyl-*p*-phenylenediamine	144 to 152
	N-*N*'-diphenylethylenediamine	60 to 65

Accelerators--As with the antidegradants, the common accelerators have melting points between 70°C and 200°C. Hence, emissions of these components are to be expected at normal curing temperatures. Average total emissions of 0.5% to 1.0% by weight of accelerator present can be anticipated (20). The melting points of the common accelerators are given in Table 25.

TABLE 25. MELTING POINTS OF COMMON ACCELERATORS (19)

Accelerator type	Compound	Melting point, °C
Dithiocarbamate	Zinc diethyldithiocarbamate	171 to 180
	Zinc dibutyldithiocarbamate	98 to 108
	Sodium dibutyldithiocarbamate	Liquid
	Selenium dimethyldithiocarbamate	140 to 172
Thiuram	Tetramethylthiuram monosulfide	103 to 108
	Tetramethylthiuram disulfide	140 to 148
	Tetraethylthiuram disulfide	62 to 75
Sulfenamide	*N*,*N*-diethyl-2-benzothiazylsulfenamide	Liquid
	N-cyclohexyl-2-benzothiazylsulfenamide	93 to 108
	N-oxydiethylene-2-benzothiazylsulfenamide	70 to 90
Thiazole	2-Mercaptobenzothiazole	164 to 176
	Benzothiazyl disulfide	160 to 176
	2-Benzothiazyl-*N*,*N*-diethylthiocarbamylsulfide	69
Guanidine	Diphenylguanidine	145 to 147
	Di-*o*-tolylguanidine	167 to 173

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(20) Angert, I. G., A. I. Zenchenki, and A. S. Kuminski. Volatilization of Phenyl-2-Naphthylamine from Rubber. Rubber Chemistry and Technology, 34(3):807, 1961.

Processing Aids and Diluents--Processing aids are generally in the form of oils (usually paraffinic) and function as lubricants, plasticizers, and softeners. Diluents are primarily aromatic extender oils used to improve the overall performance of synthetic rubbers. Volatilization from these mixtures is expected to vary considerably depending on their composition. Available data show that the total emissions in 3 hours at 167°C range from 0.05% to 1.0% by weight (21).

Miscellaneous Compounding Ingredients--The materials in this category which are most likely to be volatilized are the vulcanizing agents and retarders. These substances include amines, esters, and organic acids, most of which are either liquids at room temperature or solids with melting points between 70°C and 200°C. Emissions of the order of 1% by weight can be expected (19).

In nearly all cases, the materials used in rubber blends are of technical grade. Hence, the purity of the principal component is low (60% to 95%), and some of the impurities will be sufficiently volatile to be emitted during curing. The wide melting point ranges of many of the compounds given above are indicative of high impurity levels. Gas chromatographic analysis of commercial antioxidants has confirmed the high impurity levels in these compounds (22). As a result, there are hundreds of compounds which may be emitted in trace amounts during the curing operation.

The volatilization of components from rubber stock during cure has been shown to follow the theoretical equation (20):

$$c = c_o \left(1 - e^{-mt'/R} \right) \tag{2}$$

where c = amount of component lost in time, t, percent by weight of rubber
c_o = initial concentration of component, weight percent
m = a constant which depends on the diffusion coefficient of the species at the curing temperature
R = thickness of rubber stock
t' = time

Thus, physical losses of particular ingredients are related exponentially to the temperature and duration of cure, stock thickness, and individual diffusion coefficients.

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(21) Taft, W. K., M. Felton, J. Duke, R. W. Laundrie, and D. C. Prem. Oil Types in the Program for Oil Extended Rubber Industrial and Engineering Chemistry, 47(5):1077, 1955.

(22) Gaeta, L. J., et al. Antioxidant Analysis. Rubber Age, 101(6):47, 1967.

Upon mixing with general plant air, some of the vaporized organic materials are condensed into either oil mists or solid particles, resulting in particulate emissions.

Rubber Footwear

Sources of emission in a rubber footwear plant are the 1) compounding, 2) milling, 3) calendering, 4) molding, 5) rubber cementing, 6) latex dipping and drying, and 7) curing operations.

Emissions from compounding, milling, and calendering operations have been mentioned earlier in this section for tire manufacturing. The only difference is that the compounding operation in footwear plants involves lower temperatures than those used in tire plants. This results in lower hydrocarbon emissions. Molding of the soles has hydrocarbon emissions similar to those from tire curing due to the heat applied to the rubber material. In addition, particulates are formed and emitted as a result of condensation of hydrocarbon vapor from high-temperature molding operations.

Rubber cementing operations are performed for various purposes, including combination of fabric sheets, molded outsole cementing, sole lining, basket sole cementing, etc. Cementing is usually accomplished by hand application, and solvents contained in the cement mixture are evaporated to the general work area and vented to the outside atmosphere by the ventilation system.

After the various components have been attached together, the shoes are partially or entirely dipped in latex and dried, either by air or in an oven. The finished shoes are then cured in an air-heated autoclave, which is vented to the plant exterior. These are sources of hydrocarbon emissions. The possible volatilized chemical substances and particulate emissions from the curing operation have been described earlier in this section.

Rubber Hose and Belting

Sources of emissions from manufacturing of rubber hose and belting are the 1) compounding, 2) milling, 3) calendering, 4) extrusion, 5) fabric cementing, 6) rubber cementing, and 7) curing operations.

Particulate and hydrocarbon emissions from compounding, milling, calendering, and extrusion operations are similar to those mentioned earlier for the tire industry. Emissions from fabric cementing and rubber cementing are from evaporation of solvents which are used as the vehicle for application of the adhesive materials.

In most of the curing operations in this industry a batch steam autoclave is used and some hydrocarbons vaporized during vulcanization are condensed with the steam prior to venting to the plant exterior. This reduces hydrocarbon and particulate emissions but generates a water pollution problem.

Fabricated Rubber Products, N.E.C.

Emission sources in this industry include the 1) compounding, 2) milling, 3) calendering, 4) extrusion, 5) bonding of extruded parts, 6) latex dipping and drying, 7) adhesive spraying, 8) molding, and 9) curing operations.

Emissions from compounding, milling, calendering, extrusion, and latex dipping and drying have been mentioned previously. Emissions from the bonding of extruded parts are hydrocarbons from evaporation of solvents which are used for lubrication and for tackifying the rubber parts. Solvent hydrocarbons are also emitted during the spraying of adhesive which is applied to metal surfaces before the molding operation in the production of metal-bonded items. Dry metal screen filters are usually used for the exhaust from adhesive spraying booths to catch the adhesive aerosols. Evaporated solvents are then vented to the atmosphere.

Particulate and hydrocarbon emissions from the molding operation are similar to those from the curing operation in tire manufacturing. The curing of extruded products is usually performed in a batch autoclave. Some oil mists, most of the solid particles, and steam are condensed before venting to the atmosphere.

Metal degreasing operations are another source of hydrocarbon emissions. These operations are performed to prepare the metal surfaces before adhesive spraying. This source is not considered in this assessment because it is covered by another report entitled "Source Assessment: Solvent Evaporation - Degreasing" (23).

Gaskets, Packing, and Sealing Devices

Emission sources in this industry include 1) compounding, 2) milling, 3) calendering, 4) adhesive spraying, and 5) molding. The materials emitted from these operations are similar to those from the production of general molded products as discussed in the preceding subsection.

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(23) Marn, P. J., T. J. Hoogheem, D. A. Horn, and T. W. Hughes. Source Assessment: Solvent Evaporation - Degreasing. Contract 68-02-1874, U.S. Environmental Protection Agency, Cincinnati, Ohio. (Final document submitted to EPA by Monsanto Research Corporation, January 1977.) 180 pp.

Rubber Wire-Insulating

Sources of emissions in this industry include: 1) compounding, 2) milling, 3) extrusion, and 4) curing. Materials emitted from compounding, milling, and extrusion are similar to those from other rubber product industries.

In the continuous curing of insulated wire, since the curing device is enclosed, volatilized hydrocarbons are condensed with steam and contained in the condensate (4). Fugitive emissions from the curing operation itself occur from the curing tube (4). When the insulated wire exits from the curing tube, the rubber material is still hot, and it is depressurized. This results in another source of hydrocarbon emission. In this assessment, the above two sources are considered as emissions from the curing operation.

Tire Retreading

Emission sources in tire retreading include 1) buffing, 2) rubber cementing, 3) curing, and 4) finish painting.

The buffing operation is performed by using a grinding wheel to remove the remaining tread and is a source of particulate emissions. Rubber cementing is usually done in a spray booth. Hydrocarbons are emitted from evaporation of solvents in the cement mixture. Emissions of hydrocarbons and particulates from curing operations in retreading are substantially less than those in new tire manufacturing, because only the new tread is "green," or unvulcanized. In the finish painting operations, both water-based and solvent-based coating solutions are used. Hydrocarbons are emitted only when solvent-based solutions are applied.

EMISSION FACTORS

The quantities of materials emitted per unit of production are reported here for uncontrolled emissions and for emissions from average plants. The uncontrolled emission factors were obtained from, or derived from information contained in literature sources and Government reports. The representative emission factors (for average plants) were derived so that they can be used to calculate mass emissions and ambient pollutant concentrations by multiplying with the production figure.

In the derivation of representative emission factors, E_r, the following were considered: 1) uncontrolled emission factors for each unit operation in the industry, E_u; 2) the utilization factor (extent of utilization) of the unit operation in the whole industry, U (in percent); and 3) the generally achieved control efficiency for the unit operation representing current control practices in the industry, C (in percent). The representative emission factor was thus calculated by the following formula:

$$E_r = E_u \left(\frac{U}{100}\right)\left(1 - \frac{C}{100}\right) \qquad (3)$$

Emission factors are given in Tables 26 through 35 for 1) SBR production by emulsion polymerization; 2) SBR production by solution polymerization; 3) reclaimed rubber production; 4) tires and inner tubes; 5) rubber footwear; 6) rubber hose and belting; 7) fabricated rubber products, N.E.C.; 8) gaskets, packing, and sealing devices; 9) rubber wire-insulating; and 10) tire retreading. Blanks in the tables indicate no emissions of particular pollutants from those unit operations. Sources of information are indicated by the reference numbers in parentheses following the corresponding quantities presented. The derivation of the process utilization factor for each industry is explained by footnotes in the respective tables. A detailed description of control technologies and control efficiencies used in these tables are given in Section 5.

ENVIRONMENTAL EFFECTS

Definition of Representative Plants

For the purpose of assessing the source severity for the rubber processing industries, a representative plant was defined for each of the 9 SIC's, except SIC 2822. In SIC 2822, it was found that two representative plants are necessary because the two processes used, emulsion polymerization and solution polymerization, have different emission characteristics. The factors considered in defining these representative plants are annual production, emission factors, emission heights, population density, and wind velocity around the plant.

For SIC's 2822, 3021, 3031, 3041, and 3357, the annual production for representative plants was obtained by dividing the 1975 total national production (as presented in Tables 6 and 7) by the total number of plants (as shown in Table 23). For SIC 3011 (Tires and Inner Tubes), the representative plant was defined for tire production only, since this segment of the industry represents 93% of the product shipments in the SIC, with inner tubes, tread rubber, tire sundries, and repair materials constituting only 7% of the industry economy. The average (representative) annual production was obtained by dividing the 1975 total production by the number of tire plants (24). For SIC's 3069 and 3293, about 50% of total plants are small ones, with less than 20 employes producing less than 5% of goods in the respective industries (15). Therefore, only those plants having more than 20 employes were considered in obtaining the average annual production. For SIC 7534 (Tire Retreading), owing to lack of data on the total

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(24) A Look at the Tire Industry. Rubber World, 175(4):42-46, 1977.

TABLE 26. EMISSION FACTORS FOR SBR PRODUCTION BY EMULSION POLYMERIZATION (SIC 2822)[a]

	Uncontrolled emission factors, g/kg product				Process utilization factor,[b] %	Control efficiency,[c] %	Representative emission factors, g/kg product			
	Criteria pollutants		Chemical substances				Criteria pollutants		Chemical substances	
Emission source	Hydrocarbons	Particulates	Styrene	Butadiene			Hydrocarbons	Particulates	Styrene	Butadiene
Styrene storage (breathing)	0.02 (4)		0.02 (16)		100	0	0.02		0.02	
Styrene storage (fugitive)	0.04 (4)		0.04 (16)		100	0	0.04		0.04	
Reactor section (fugitive)	0.4 (4)		-[d]	-[d]	100	0	0.4		-[e]	-[e]
Butadiene absorption	2.5 (4)		-[d]	0.1 (16)	100	0	2.5		-[e]	0.1
Monomer recovery area (fugitive)	0.1 (4)		-[d]	-[d]	100	0	0.1		-[e]	-[e]
Carbon black application		1.0 (16)			85[f]	70		0.3		
Drying	0.6 (4)	0.02 (16)	0.6 (16)	-[d]	85[f]	0	0.5	0.02	0.5	-[e]
Baling		0.1 (16)			85[f]	70		0.03		
TOTAL	N.A.[g]	N.A.	N.A.	N.A.	N.A.	N.A.	3.6	0.35	-[e]	-[e]

[a] Blanks indicate no emissions from unit operations. Numbers in parentheses indicate sources of data (references).

[b] This represents the extent of utilization of a particular unit operation in the whole industry.

[c] This is the control efficiency for the emissions from the unit operation which represents current control practices in the industry. See Section IV for details.

[d] Data for specific emissions were not available.

[e] Not calculated due to lack of data.

[f] This is the percentage for crumb rubber production and represents the portion of the industry that utilizes the corresponding unit operations.

[g] Not applicable.

TABLE 27. EMISSION FACTORS FOR SBR PRODUCTION BY SOLUTION POLYMERIZATION (SIC 2822)[a]

Emission source	Uncontrolled emission factors, g/kg product					Process utilization factor,[b] %	Control efficiency,[c] %	Representative emission factors, g/kg product				
	Criteria pollutants		Chemical substances					Criteria pollutants		Chemical substances		
	Hydrocarbons	Particulates	Styrene	Butadiene	Hexane			Hydrocarbons	Particulates	Styrene	Butadiene	Hexane
Styrene storage (breathing)	0.02 (4)		0.02 (4)			100	0	0.02		0.02		
Hexane storage (breathing)	0.05 (4)				0.05	100	0	0.05				0.05
Storage area (fugitive)	0.04 (4)		-[d]	-[d]	-[d]	100	0	0.04		-[e]	-[e]	-[e]
Reactor area (fugitive)	0.4 (4)		-[d]	-[d]	-[d]	100	0	0.4		-[e]	-[e]	-[e]
Carbon black application		1.0 (16)				100	70		0.3			
Desolvent area (surge vent)	2.7 (4)		-[d]	-[d]	-[d]	100	50	1.4		-[e]	-[e]	-[e]
Desolvent area (fugitive)	0.2 (4)		-[d]	-[d]	-[d]	100	0	0.2		-[e]	-[e]	-[e]
Purification area (fugitive)	0.2 (4)		-[d]	-[d]	-[d]	100	0	0.2		-[e]	-[e]	-[e]
Drying	17.1 (4)	0.02 (16)			15.3 (4)	100	0	17.1	0.02			15.3
Baling		0.1 (16)				100	70		0.03			
TOTAL	N.A.[f]	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	19.1	0.35	-[e]	-[e]	-[e]

[a] Blanks indicate no emissions from unit operations. Numbers in parentheses indicate sources of data (references).

[b] Represents the extent of utilization of a particular unit operation in the whole industry.

[c] Control efficiency for emissions from the unit operation which represents current control practices in the industry. See Section IV for details.

[d] Data for specific emissions not available.

[e] Not calculated due to lack of data.

[f] Not applicable.

TABLE 28. EMISSION FACTORS FOR RUBBER RECLAIMING (SIC 3031)[a]

Emission source	Uncontrolled emission factors, g/kg product		Process utilization factor,[b] %	Control efficiency,[c] %	Representative emission factors, g/kg product	
	Hydrocarbons	Particulates			Hydrocarbons	Particulates
Size reduction		5.0[d]	100	80		1.0
Depolymerization	30 (4)		100	90	3.0	
Baling		0.1[e]	100	0		0.1
TOTAL	N.A.[f]	N.A.	N.A.	N.A.	3.0	1.1

[a] Blanks indicate no emissions from unit operation. Numbers in parentheses indicate sources of data (references).

[b] Represents the extent of utilization of a particular unit operation in the whole industry.

[c] Control efficiency for emissions from the unit operation which represents current control practices in the industry. See Section IV for details.

[d] Estimated from engineering experience.

[e] Assumed to be the same as in SBR production.

[f] Not applicable.

TABLE 29. EMISSION FACTORS FOR TIRES AND INNER TUBES (SIC 3011)[a]

Emission source	Uncontrolled emission factors, g/kg product		Process utilization factor,[b] %	Control efficiency,[c] %	Representative emission factors, g/kg product	
	Hydrocarbons	Particulates			Hydrocarbons	Particulates
Compounding	0.3 (4)	11 (25)	100	0[d], 90[e]	0.3	1.1
Milling	0.2 (4)		100	0	0.2	
Calendering	0.2 (4)		100	0	0.2	
Fabric cementing	5.0 (4)		100	85	0.8	
Extrusion	0.2 (4)		100	0	0.2	
Undertread cementing	2.8 (4)		100	65	1.0	
Green tire spraying	14 (4)		100	40	8.4	
Curing	5.0 (4)	2.5[f]	100	0	5.0	2.5
TOTAL	N.A.[g]	N.A.	N.A.	N.A.	16.1	3.6

[a] Blanks indicate no emissions from unit operation. Numbers in parentheses indicate sources of data (references).

[b] Represents the extent of utilization of a particular unit operation in the whole industry.

[c] Control efficiency for emissions from the unit operation which represents current control practices in the industry. See section IV for details.

[d] For hydrocarbons.

[e] For particulates.

[f] Assume 50% of emitted hydrocarbons is condensed into oil mists or solid organic particles.

[g] Not applicable.

TABLE 30. EMISSION FACTORS FOR RUBBER FOOTWEAR (SIC 3021)[a]

Emission source	Uncontrolled emission factors, g/kg product: Hydrocarbons	Uncontrolled emission factors, g/kg product: Particulates	Process utilization factor,[b] %	Control efficiency,[c] %	Representative emission factors, g/kg product: Hydrocarbons	Representative emission factors, g/kg product: Particulates
Compounding	0.3 (4)	11 (25)	100	0[d], 90[e]	0.3	1.1
Milling	0.2 (4)		100	0	0.2	
Calendering	0.2 (4)		100	0	0.2	
Molding	4.0 (4)	2.0[f]	50	0	2.0	1.0
Rubber cementing	95 (4)		100	0	95	
Latex dipping and drying	0.4 (4)		25	0	0.1	
Curing	3.0 (4)	1.5[f]	50	0	1.5	0.8
TOTAL	N.A.[g]	N.A.	N.A.	N.A.	99.3	2.9

[a] Blanks indicate no emissions from unit operation. Numbers in parentheses indicate sources of data (reference).

[b] Represents the extent of utilization of a particular unit operation in the whole industry.

[c] Control efficiency for emissions from the unit operation which represents current control practices in the industry. See Section IV for details.

[d] For hydrocarbons.

[e] For particulates.

[f] Assume 50% of emitted hydrocarbons is condensed into oil mists or solid organic particles.

[g] Not applicable.

TABLE 31. EMISSION FACTORS FOR RUBBER HOSE AND BELTING (SIC 3041)[a]

Emission source	Uncontrolled emission factors, g/kg product: Hydrocarbons	Uncontrolled emission factors, g/kg product: Particulates	Process utilization factor,[b] %	Control efficiency,[c] %	Representative emission factors, g/kg product: Hydrocarbons	Representative emission factors, g/kg product: Particulates
Compounding	0.3 (4)	11 (25)	100	0[d], 90[e]	0.3	1.1
Milling	0.2 (4)		100	0	0.2	
Calendering	0.2 (4)		100	0	0.2	
Extrusion	0.03 (4)		50	0	0.02	
Fabric cementing	25 (4)		50	85	1.9	
Rubber cementing	1.0 (4)		100	0	1.0	
Curing	3.0 (4)		100	0	3.0	
TOTAL	N.A.[f]	N.A.	N.A.	N.A.	6.6	1.1

[a] Blanks indicate no emissions from unit operation. Numbers in parentheses indicate sources of data (reference).

[b] Represents the extent of utilization of a particular unit operation in the whole industry.

[c] Control efficiency for emissions from the unit operation which represents current control practices in the industry. See Section IV for details.

[d] For hydrocarbons.

[e] For particulates.

[f] Not applicable.

TABLE 32. EMISSION FACTORS FOR FABRICATED RUBBER PRODUCTS, N.E.C. (SIC 3069)[a]

Emission source	Uncontrolled emission factors, g/kg product		Process utilization factor,[b] %	Control efficiency,[c] %	Representative emission factors, g/kg product	
	Hydrocarbons	Particulates			Hydrocarbons	Particulates
Compounding	0.3 (4)	11 (25)	100	0[d], 90[e]	0.3	1.1
Milling	0.2 (4)		75	0	0.15	
Calendering	0.2 (4)		75	0	0.15	
Extrusion	0.06 (4)		50	0	0.03	
Bonding of extruded parts	2.0 (4)		10	0	0.2	
Latex dipping and drying	0.5 (4)		25	0	0.13	
Adhesive spraying	1.8 (4)		100	0	1.8	
Molding	4.0 (4)	2.0[f]	40	0	1.6	2.0
Curing	3.0 (4)		60	0	1.8	
TOTAL	N.A.[g]	N.A.	N.A.	N.A.	6.2	3.1

[a] Blanks indicate no emissions from unit operation. Numbers in parentheses indicate sources of data (reference).

[b] Represents the extent of utilization of a particular unit operation in the whole industry.

[c] Control efficiency for emissions from the unit operation which represents current control practices in the industry. See Section IV for details.

[d] For hydrocarbons.

[e] For particulates.

[f] Assume 50% of emitted hydrocarbons is condensed into oil mists or solid organic particles.

[g] Not applicable.

TABLE 33. EMISSION FACTORS FOR GASKETS, PACKING, AND SEALING DEVICES (SIC 3293)[a]

Emission source	Uncontrolled emission factors, g/kg product		Process utilization factor,[b] %	Control efficiency,[c] %	Representative emission factors, g/kg product	
	Hydrocarbons	Particulates			Hydrocarbons	Particulates
Compounding	0.3 (4)	11 (25)	100	0[d], 90[e]	0.3	1.1
Milling	0.2 (4)		100	0	0.2	
Calendering	0.2 (4)		100	0	0.2	
Adhesive spray	3.6 (4)		100	0	3.6	
Molding	4.0 (4)	2.0[f]	100	0	4.0	2.0
TOTAL	N.A.[g]	N.A.	N.A.	N.A.	8.3	3.1

[a] Blanks indicate no emissions from unit operation. Numbers in parentheses indicate sources of data (reference).

[b] Represents the extent of utilization of a particular unit operation in the whole industry.

[c] Control efficiency for emissions from the unit operation which represents current control practices in the industry. See Section IV for details.

[d] For hydrocarbons.

[e] For particulates.

[f] Assume 50% of emitted hydrocarbons is condensed into oil mists or solid organic particles.

[g] Not applicable.

TABLE 34. EMISSION FACTORS FOR RUBBER WIRE-INSULATING (SIC 3357)[a]

Emission source	Uncontrolled emission factors, g/kg product: Hydrocarbons	Uncontrolled emission factors, g/kg product: Particulates	Process utilization factor,[b] %	Control efficiency,[c] %	Representative emission factors, g/kg product: Hydrocarbons	Representative emission factors, g/kg product: Particulates
Compounding	0.3 (4)	11 (25)	100	0[d], 90[e]	0.3	1.1
Milling	0.2 (4)		100	0	0.2	
Extrusion	0.03 (4)		100	0	0.03	
Curing	3.0 (4)		100	0	3.0	
TOTAL	N.A.[f]	N.A.	N.A.	N.A.	3.5	1.1

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[a] Blanks indicate no emissions from unit operation. Numbers in parentheses indicate sources of data (reference).

[b] Represents the extent of utilization of a particular unit operation in the whole industry.

[c] Control efficiency for emissions from the unit operation which represents current control practices in the industry. See Section IV for details.

[d] For hydrocarbons.

[e] For particulates.

[f] Not applicable.

TABLE 35. EMISSION FACTORS FOR TIRE RETREADING (SIC 7534)[a]

Emission source	Uncontrolled emission factors, g/kg product: Hydrocarbons	Uncontrolled emission factors, g/kg product: Particulates	Process utilization factor,[b] %	Control efficiency,[c] %	Representative emission factors, g/kg product: Hydrocarbons	Representative emission factors, g/kg product: Particulates
Buffing		20 (4)	100	90		2.0
Rubber cementing	3.0 (4)		100	0	3.0	
Curing	0.8 (4)		100	0	0.8	
Finish painting	0.8 (4)		50	0	0.4	
TOTAL	N.A.[d]	N.A.	N.A.	N.A.	4.2	2.0

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[a] Blanks indicate no emissions from unit operation. Numbers in parentheses indicate sources of data (reference).

[b] Represents the extent of utilization of a particular unit operation in the whole industry.

[c] Control efficiency for emissions from the unit operation which represents current control practices in the industry. See Section IV for details.

[d] Not applicable.

number of plants and the plant size distribution, an annual production of 40,000 tires (450 metric tons/yr of product) was assumed and used for the representative plant. The annual production for representative plants is summarized in Table 36.

TABLE 36. PARAMETERS USED TO DEFINE THE REPRESENTATIVE PLANTS

Population density around the plant = 103 persons/km^2
Wind velocity around the plant = 4.5 m/s

Industries	Annual production, metric tons/yr	Emission height, m
SBR by emulsion (SIC 2822)	41,000	20
SBR by solution (SIC 2822)	41,000	20
Rubber reclaiming (SIC 3031)	14,000	20
Tires and inner tubes (SIC 3011)	20,000	15
Rubber footwear (SIC 3021)	2,700	15
Hose and belting (SIC 3041)	6,500	15
Fabricated products, N.E.C. (SIC 3069)	1,700	15
Gaskets, packing, and sealing devices (SIC 3293)	1,700	15
Wire insulating (SIC 3357)	3,000	15
Tire retreading (SIC 7534)	450	15

The representative emission factors as defined earlier in this section and presented in Tables 26 through 35 were used for the representative plants. The process utilization factor and the generally achieved control efficiency for each operation which are also given in the above tables, are applicable to the definition of representative plants.

Assumed emission heights of 20 m and 15 m were based on a NEDS Point Source Listing[a] and engineering judgment for elastomer production and rubber products fabrication, respectively. All emissions in a plant were assumed to occur at the same height, based on the assumption that fugitive emissions do not escape through doors, windows, etc., but eventually travel through the plant ventilation system to be discharged through the representative stack.

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[a] Point Source Listings are provided by EPA from the National Emissions Data System (NEDS) via AEROS (26).

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(26) Aerometric and Emissions Reporting System (AEROS), U.S. Environmental Protection Agency. National Air Data Branch, Research Triangle Park, North Carolina 27711.

The population density around a representative plant was assumed to be 103 persons/km^2. This is the composite state population density derived and given in Section 3. For the wind velocity, the national average of 4.5 m/s was used.

Source Severity

In order to obtain a quantitative measure of the hazard potential of rubber processing, the source severity, S, is defined as:

$$S = \frac{\overline{\chi}_{max}}{F} \qquad (4)$$

where $\overline{\chi}_{max}$ is the time-averaged maximum ground level concentration of each pollutant emitted from a representative plant, and F is defined as a primary ambient air quality standard for criteria pollutants (particulate and hydrocarbons in this case), while for noncriteria pollutants:

$$F \equiv TLV \cdot 8/24 \cdot 0.01,\ g/m^3 \qquad (5)$$

The factor 8/24 adjusts the TLV® (27) for continuous rather than workday exposure, and the factor of 0.01 accounts for the fact that the general population is a higher risk group than healthy workers.

Thus, the source severity represents the ratio of the maximum mean ground level exposure to the hazard level of exposure for a given pollutant.

The maximum ground level concentration, χ_{max}, is calculated according to Gaussian plume dispersion theory (28):

$$\chi_{max} = \frac{2\ Q}{\pi H^2 e \overline{u}} \qquad (6)$$

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(27) TLVs® Threshold Limit Values for Chemical Substances and Physical Agents in the Workroom Environment with Intended Changes for 1976. American Conference of Governmental Industrial Hygienists, Cincinnati, Ohio, 1976. 94 pp.

(28) Turner, D. B. Workbook of Atmospheric Dispersion Estimates. Public Health Service Publication No. 999-AP-26, U.S. Department of Health, Education, and Welfare, Cincinnati, Ohio, May 1970. 84 pp.

where Q = mass emission rate, g/s
$\bar{u}$ = average wind speed, m/s
H = effective emission height, m
e = 2.72

Equation 6 yields a value for a short-term averaging time during which the Gaussian plume dispersion equation is valid. The short-term averaging time was found to be three minutes in a study of published data on lateral and vertical diffusion (29). For a continuously emitting source, the maximum mean ground level concentration for time intervals between three minutes and 24 hours can be estimated from the relation (28):

$$\bar{\chi}_{max} = \chi_{max}\left(\frac{t_o}{t}\right)^{0.17} \quad (7)$$

where t_o = short-term averaging time (3 min)
t = averaging time

For noncriteria pollutants, the averaging time, t, is 24 hours. For criteria pollutants, the averaging times are those used in the definition of the primary ambient air quality standards. Insertion of the national average wind speed of 4.5 m/s and the primary air quality standards with corresponding averaging times for hydrocarbons and particulates leads to the following severity equations:

$$\text{for hydrocarbons, } S = 162.5\ QH^{-2} \quad (8)$$

$$\text{for particulates, } S = 70\ QH^{-2} \quad (9)$$

where Q and H are expressed in the units of g/s and m, respectively, a detailed derivation of the above two equations is given in Appendix A.

For noncriteria pollutants (chemical substances), insertion of Equations 5, 6, and 7 into Equation 4, using 24 hours as the averaging time, gives the following:

$$S = 5.5\ QH^{-2}(TLV)^{-1} \quad (10)$$

where TLV (threshold limit value) is in the units of g/m^3 and Q and H have the same units as those for Equations 8 and 9.

The primary ambient air quality standards and TLV's used in the calculation of source severities are given in Table 37.

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(29) Nonhebel, G. Recommendations on Heights for New Industrial Chimneys. Journal of the Institute of Fuel. 33:479-511, July 1960.

TABLE 37. PRIMARY AMBIENT AIR QUALITY STANDARDS AND THRESHOLD LIMIT VALUES FOR POLLUTANTS CONSIDERED

Pollutant species	AAQS, mg/m^3 (30)	TLV, mg/m^3 (27)
Hydrocarbons	0.16	N.A.[a]
Particulates	0.26	N.A.
Styrene	N.A.	420
Butadiene	N.A.	2,200
Hexane	N.A.	360

[a] Not applicable.

Using the parameters given in the definition of representative plants and the above equations, source severities were calculated for emission points within the representative plants. These source severities are presented in Table 38 for industries in elastomer production, and in Table 39 for industries in rubber products fabrication.

Except for SIC 3011 (Tires and Inner Tubes), particulate emissions result in source severities of less than 0.1 from all industries. SIC's 3031, 3041, 3293, and 3357 have at least one hydrocarbon emission point which has a source severity between 0.1 and 1.0. SIC's 2822 (both emulsion and solution polymerization), 3011, and 3021 have at least one emission point with hydrocarbon source severity greater than 1.0. All the hydrocarbon emission points in SIC's 3069 and 7534 have source severities less than 0.1. In addition, except for hexane from solution polymerization known emissions of all noncriteria pollutants all have source severities less than 0.1.

Affected Population

A measure of the population which is exposed to a high contaminant concentration due to emissions from a representative rubber processing plant can be obtained as follows. The values of x, downwind distance from the source, for which

$$\frac{\overline{\chi}(x)}{F} = 0.1 \text{ or } 1.0 \qquad (11)$$

are determined by iteration. The value of $\overline{\chi}(x)$, the annual mean ground level concentration, is computed from the equation (28):

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(30) Code of Federal Regulations, Title 42 - Public Health, Chapter IV - Environmental Protection Agency, Part 410 - National Primary and Secondary Ambient Air Quality Standards, April 28, 1971. 16 pp.

TABLE 38. SOURCE SEVERITIES FOR REPRESENTATIVE ELASTOMER PLANTS[a]

	SBR Emulsion polymerization (SIC 2822)				SBR Solution polymerization (SIC 2822)					Rubber recla'ming (SIC 3031)	
	Criteria pollutants		Chemical substances		Criteria pollutants		Chemical substances			Criteria pollutants	
Emission source	Hydro-carbons	Particu-lates	Styrene	Butadiene	Hydro-carbons	Particu-lates	Styrene	Butadiene	Hexane	Hydro-carbons	Particu-lates
Styrene storage (breathing)	0.01		0.001		0.01		0.001				
Hexane storage (breathing)					0.03				0.002		
Storage area (fugitive)	0.02		0.002		0.02		–[b]	–[b]	–[b]		
Reactor area (fugitive)	0.2		–[b]	–[b]	0.2		–[b]	–[b]	–[b]		
Butadiene absorption	1		–[b]	0.001							
Monomer recovery area (fugitive)	0.05		–[b]	–[b]							
Desolvent area (surge vent)					0.7		–[b]	–[b]	–[b]		
Desolvent area (fugitive)					0.1		–[b]	–[b]	–[b]		
Purification area (fugitive)					0.1		–[b]	–[b]	–[b]		
Carbon black application		0.07				0.07					
Size reduction											0.08
Depolymerization										0.5	
Drying	0.3	0.005	0.02	–[b]	9	0.005			0.8		
Baling		0.007				0.007					0.008

[a] Blanks indicate no emissions from unit operations.

[b] Not calculated due to lack of data.

TABLE 39. SOURCE SEVERITIES FOR REPRESENTATIVE RUBBER PRODUCT PLANTS[a]

Emission source	SIC 3011		SIC 3021		SIC 3041		SIC 3069		SIC 3293		SIC 3357		SIC 7534	
	Hydro-carbons	Particu-lates	Hydro-carbons	Particu-lates	Hydro-carbons	Particu-lates	Hydro-carbons	Particu-lates	Hydro-carbons	Particu-lates	Hydro-carbons	Particu-lates	Hydro-carbons	Particu-lates
Compounding	0.1	0.2	0.02	0.03	0.04	0.07	0.01	0.02	0.01	0.02	0.02	0.03		
Milling	0.09		0.01		0.03		0.006		0.008		0.01			
Calendering	0.09		0.01		0.03		0.006		0.008					
Fabric cementing	0.4				0.3									
Extrusion	0.09				0.003		0.001				0.002			
Undertrade cementing	0.4													
Green tire spraying	4													
Buffing														0.01
Rubber cementing			6		0.1								0.03	
Latex dipping and drying			0.01				0.005							
Bonding of extruded parts							0.008							
Adhesive spraying							0.07		0.1					
Molding			0.1	0.03			0.06	0.03	0.2	0.03				
Curing	2	0.5	0.1	0.02	0.4		0.07				0.2		0.008	
Finish painting													0.004	

[a] Blanks indicate no emissions from unit operations.

$$\overline{\chi}(x) = \frac{2.03\ Q}{\sigma_z \overline{u} x} \exp\left[-\frac{1}{2}\left(\frac{H}{\sigma_z}\right)^2\right] \qquad (12)$$

where Q = emission rate, g/s
H = effective emission height, m
x = downwind distance from source, m
$\overline{u}$ = average wind speed (4.5 m/s)
σ_z = vertical dispersion coefficient, m

For atmospheric stability class C (neutral conditions), σ_z is given by (31):

$$\sigma_z = 0.113(x^{0.911}) \qquad (13)$$

The affected area is then computed as

$$A = \pi(x_2{}^2 - x_1{}^2),\ \text{km}^2 \qquad (14)$$

where x_1 and x_2 are the two roots of Equation 11.

The product of affected area (A) and a composite population density ($\overline{D}$, defined and derived in Section 3) thus give the "affected population."

The affected population was computed for each pollutant and each emission point for which the source severity, S, exceeds 0.1. The results are presented in Table 40. SIC's 3069 and 7534 were not included because they do not have emissions with source severity greater than 0.1. The largest population affected is 4,000 persons exposed to the value of $\overline{\chi}(x)/F$ greater than 0.1, by the drying operation from solution polymerization segment of SIC 2822.

Contribution to Total Air Emissions

The contribution of rubber processing to statewide and nationwide air emissions was measured by the ratio of mass emissions from this source to the total emissions from all sources.

The mass emissions of hydrocarbons and particulates resulting from elastomer production and rubber products fabrication were calculated using the representative emission factors from Tables 26 through 35 and the annual production data given in

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(31) Eimutis, E. C., and M. G. Konicek. Derivations of Continuous Functions of the Lateral and Vertical Atmospheric Dispersion Coefficients. Atmospheric Environment, 6(11): 859-863, 1972.

TABLE 40. AFFECTED POPULATION BY REPRESENTATIVE RUBBER PROCESSING PLANTS[a] (number of persons)

	SIC 2822						SIC 3031	
	Emulsion		Solution					
	Hydrocarbons		Hydrocarbons		Hexane		Hydrocarbons	
	where $\chi/F>1$	where $\chi/F>0.1$	where $\chi/F>1$	where $\chi/F>0.1$	where $\chi/F>1$	where $\chi/F>0.1$	where $\chi/F>1$	where $\chi/F>0.1$
Reactor area (fugitive)	0	50	0	50				
Butadiene absorption	20	500						
Desolvent area (surge vent)			0	200				
Depolymerization							0	200
Drying	0	70	300	4,000	0	400		
Compounding								
Fabric cementing								
Under tread cementing								
Green tire spraying								
Rubber cementing								
Adhesive spraying								
Molding								
Curing								

	SIC 3011				SIC 3021		SIC 3041		SIC 3293		SIC 3357	
	Hydrocarbons		Particulates		Hydrocarbons		Hydrocarbons		Hydrocarbons		Hydrocarbons	
	where $\chi/F>1$	where $\chi/F>0.1$	where $\chi/F>1$	where $\chi/F>0.1$	where $\chi/F>1$	where $\chi/F>0.1$	where $\chi/F>1$	where $\chi/F>0.1$	where $\chi/F>1$	where $\chi/F>0.1$	where $\chi/F>1$	where $\chi/F>0.1$
Reactor area (fugitive)												
Butadiene absorption												
Desolvent area (surge vent)												
Depolymerization												
Drying												
Compounding		10	0	60								
Fabric cementing		60					0	40				
Under tread cementing		80										
Green tire spraying	60	800										
Rubber cementing					100	1,000	0	10				
Adhesive spraying									0	10		
Molding									0	20		
Curing	30	500	0	100	0	7	0	80			0	20

[a] Blanks indicate no emissions from a specific operation.

Section 3 for each SIC. The national mass emissions were obtained by multiplying appropriate emission factors by the total annual production. State emissions were obtained by distributing the national emissions among the states according to the number of plants in the applicable states.

The nationwide mass emissions and percent contribution of hydrocarbons and particulates for each SIC are presented in Table 41. The mass emissions from each state are given in Appendix B. The percent contributions of hydrocarbons and particulates from rubber processing to the corresponding total state emissions are shown in Tables 42 and 43. The total pollutant emissions nationwide and for each state from all sources which were used for above calculations were obtained from the 1972 National Emissions Report (32).

TABLE 41. NATIONWIDE EMISSIONS OF CRITERIA POLLUTANTS FROM RUBBER PROCESSING INDUSTRIES

Industries	Mass emission, metric tons/yr		Percent contribution	
	Hydrocarbons	Particulates	Hydrocarbons	Particulates
SBR production (SIC 2822)	6,000[a]	410[b]	0.024	0.0023
Rubber reclaiming (SIC 3031)	250	91	0.0010	0.0005
Tires and inner tubes (SIC 3011)	33,000	7,300	0.13	0.041
Rubber footwear (SIC 3021)	14,000	400	0.056	0.0022
Hose and belting (SIC 3041)	2,600	440	0.010	0.0025
Fabricated Products, N.E.C. (SIC 3069)	6,200	3,100	0.025	0.017
Gaskets, packing, and sealing devices (SIC 3293)	1,300	500	0.0052	0.0028
Wire insulating (SIC 3357)	180	56	0.0007	0.0003
Tire retreading (SIC 7534)	2,000	950	0.0080	0.0053
TOTAL	65,500	13,200	0.26	0.074

[a] 63% of this is emitted from emulsion polymerization; the remaining 37% is from solution polymerization.

[b] 90% of this is emitted from emulsion polymerization; the remaining 10% is from solution polymerization.

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(32) 1972 National Emissions Report. EPA-450/2-74-012, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, June 1974. 422 pp.

TABLE 42. PERCENT CONTRIBUTION OF HYDROCARBON EMISSIONS FROM RUBBER PROCESSING TO TOTAL STATE EMISSIONS

State	SIC 2822	SIC 3031	SIC 3011	SIC 3021	SIC 3041	SIC 3069	SIC 3293	SIC 3357	SIC 7534[a]	State Total
Alabama			0.25			0.0095	0.0031		0.0044	0.26
Arizona			0.17			0.020			0.0053	0.19
Arkansas			0.41	0.14	0.022	0.017			0.0082	0.56
California	0.019		0.16	0.051	0.013	0.037	0.0088	0.0010	0.012	0.30
Colorado			0.25		0.022	0.0088	0.0067		0.0052	0.29
Connecticut	0.096	0.038	0.073	0.12	0.019	0.12	0.018	0.0096	0.033	0.50
Delaware	0.33		0.25		0.19	0.017			0.012	0.80
Florida			0.052	0.087		0.019	0.0011		0.0052	0.16
Georgia	0.090		0.30	0.12		0.037		0.0022	0.012	0.57
Illinois	0.012	0.0023	0.088	0.015	0.012	0.019	0.0082	0.0005	0.0066	0.16
Indiana			0.13	0.090	0.014	0.052	0.0057	0.0017	0.014	0.32
Iowa			0.25			0.0088			0.0038	0.26
Kansas			0.10						0.0006	0.10
Kentucky	0.12		0.15			0.0067	0.0021	0.0031	0.0037	0.29
Louisiana	0.032								0.0002	0.032
Maine			0.13	0.66					0.0033	0.79
Maryland			0.11	0.18		0.02	0.0044		0.0068	0.32
Massachusetts	0.093		0.22	0.36	0.027	0.082	0.014	0.0048	0.025	0.82
Michigan	0.029		0.13		0.012	0.045	0.011		0.013	0.24
Minnesota			0.039		0.010	0.032	0.0066		0.0088	0.097
Mississippi		0.021	0.24			0.031			0.0092	0.31
Missouri			0.15	0.13	0.010	0.017	0.0082		0.0073	0.31
Nebraska						0.022			0.0047	0.027
Nevada					0.16				0.0037	0.16
New Hampshire			0.54	1.2		0.012	0.0079		0.014	1.8
New Jersey			0.059	0.066	0.061	0.048	0.0090	0.0012	0.015	0.26
New York		0.0033	0.051	0.10	0.014	0.030	0.0074	0.0017	0.0095	0.22
North Carolina	0.092		0.25	0.12	0.0094	0.022	0.0045	0.0022	0.0089	0.49
Ohio	0.036	0.0036	0.37	0.070	0.036	0.084	0.010	0.0018	0.024	0.64
Oklahoma			0.32			0.011	0.0059		0.0059	0.35
Oregon			0.20			0.026			0.0068	0.24
Pennsylvania	0.046		0.25	0.14	0.014	0.030	0.0090	0.0011	0.011	0.50
Rhode Island						0.14			0.030	0.17
South Carolina			0.035		0.0046	0.0055			0.0015	0.047
South Dakota						0.0066				0.0066
Tennessee	0.11		0.58	0.22	0.012	0.020	0.0036		0.011	0.96
Texas	0.054		0.081			0.0099	0.0050		0.0039	0.15
Utah					0.043	0.028	0.013		0.010	0.095
Vermont						0.014				0.014
Virginia			0.22			0.020	0.0019		0.0060	0.24
Washington			0.093			0.0081			0.0023	0.10
West Virginia				0.23		0.038	0.011		0.010	0.29
Wisconsin			0.061	0.052		0.025	0.0065		0.0073	0.15

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[a] Blanks indicate no emissions from the industry.

[b] There is a lack of data available for complete geographical distribution of tire retreading shops. In this calculation, the percentage distribution of plants among states in this SIC was assumed to be the same as that given in Table 23 for the toal of the other eight industries.

TABLE 43. PERCENT CONTRIBUTION OF PARTICULATE EMISSIONS FROM RUBBER PROCESSING TO TOTAL STATE EMISSIONS

State	SIC 2822	SIC 3031	SIC 3011	SIC 3021	SIC 3041	SIC 3069	SIC 3293	SIC 3357	SIC 7534[a]	State Total
Alabama			0.030			0.0025	0.0007		0.011	0.034
Arizona			0.098			0.026			0.0069	0.13
Arkansas			0.13	0.0058	0.0051	0.012			0.0058	0.16
California	0.0028		0.078	0.0031	0.0050	0.040	0.0075	0.0006	0.012	0.15
Colorado			0.055		0.0035	0.0040	0.0025		0.0025	0.070
Connecticut	0.035	0.075	0.088	0.020	0.018	0.32	0.038	0.015	0.085	0.70
Delaware	0.038		0.095		0.057	0.016			0.011	0.22
Florida			0.031	0.0071		0.027	0.0009		0.0066	0.071
Georgia	0.0069		0.079	0.004		0.021		0.0070	0.0064	0.12
Illinois	0.001	0.0013	0.031	0.0007	0.0031	0.015	0.0050	0.003	0.0050	0.062
Indiana			0.024	0.0021	0.0019	0.021	0.0017	0.0004	0.0055	0.058
Iowa			0.083			0.0065			0.0028	0.10
Kansas			0.020						0.0003	0.020
Kentucky	0.0051		0.020			0.002	0.0004	0.0005	0.0011	0.029
Louisiana	0.011								0.0005	0.012
Maine			0.071	0.047					0.0041	0.12
Maryland			0.014	0.0032		0.0057	0.0010		0.0020	0.026
Massachusetts	0.029		0.22	0.048	0.022	0.19	0.024	0.0062	0.054	0.59
Michigan	0.0020		0.030		0.0020	0.023	0.0044		0.0064	0.067
Minnesota			0.013		0.0026	0.025	0.0038		0.0064	0.053
Mississippi		0.0089	0.065			0.018			0.0048	0.095
Missouri			0.069	0.0079	0.0035	0.018	0.0064		0.0069	0.11
Nebraska						0.015			0.0031	0.018
Nevada					0.015				0.0011	0.016
New Hampshire			0.74	0.21		0.034	0.013		0.040	1.0
New Jersey			0.072	0.010	0.056	0.12	0.019	0.002	0.037	0.32
New York		0.0094	0.088	0.024	0.018	0.012	0.028	0.0038	0.036	0.32
North Carolina	0.0058		0.052	0.0033	0.0015	0.010	0.0017	0.0006	0.0040	0.079
Ohio	0.0016	0.0008	0.054	0.0013	0.0040	0.027	0.0026	0.0003	0.0074	0.10
Oklahoma			0.27			0.020	0.0086		0.011	0.31
Oregon			0.065			0.018			0.0047	0.088
Pennsylvania	0.0015		0.028	0.0021	0.0012	0.0077	0.007	0.0002	0.0027	0.045
Rhode Island						0.34			0.077	0.42
South Carolina			0.036		0.0035	0.013			0.0035	0.055
South Dakota						0.0057				0.0057
Tennessee	0.0068		0.11	0.0056	0.0017	0.0088	0.0012		0.0046	0.14
Texas	0.016		0.071			0.020	0.0075		0.0075	0.12
Utah					0.0098	0.020	0.0070		0.0070	0.043
Vermont						0.021				0.021
Virginia			0.038			0.0075	0.0004		0.0021	0.048
Washington			0.044			0.0086			0.0025	0.056
West Virginia				0.0037		0.010	0.0023		0.0028	0.019
Wisconsin			0.017	0.0019		0.016	0.0032		0.0044	0.044

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[a] Blanks indicate no emissions from the industry.

[b] There is a lack of data available for complete geographical distribution of tire retreading shops. In this calculation, the percentage distribution of plants among states in this SIC was assumed to be the same as that given in Table 23 for the total of the other eight industries.

From Table 41, particulate emissions from each and even from all nine industries do not exceed 0.1% of the national emissions of the said pollutant, from all sources. The Tire and Inner Tubes industry has highest contribution of hydrocarbon emissions (over 0.1%) to the nationwide total. On a state-by-state basis, hydrocarbons from SIC 3021 (rubber footwear) exceed 1% of total emissions in New Hampshire. For the same state, total particulate emissions from the nine industries constitute 1% of the state emissions from all sources. Emissions of both pollutants, in other states contribute less than 1% of the state totals.

Growth Factor

The consumption of rubber in rubber products fabrication is expected to increase at an average simple annual rate of 3% between 1975 and 1980 (Section 6). Assuming that the production of rubber increases at the same rate and that the level of control remains the same during this period, emissions from rubber processing will increase by 15% over this period.

SECTION 5

CONTROL TECHNOLOGY

Emissions from rubber processing industries consist of hydrocarbons and particulates. Because most of the operations resulting in air emissions are not enclosed, the control of emissions from these sources involves collection of the contaminated gas and removal of the pollutants from the gas. The overall control effectiveness becomes the product of the efficiencies of the control equipment and the ventilation system.

Most rubber processing plants have some type of particulate control devices, but there are only a few operations which have hydrocarbon control equipment installed.

The best control technologies for hydrocarbons from various emission sources in the 9 rubber processing industries have been identified in Reference 4 after an extensive plant survey and engineering study. These identified best technologies for hydrocarbons and the control technologies for particulates obtained from other references are summarized, together with their efficiencies, in Tables 44 and 45 for the elastomers industry and the rubber products industry. It should be noted that the control efficiences given are for the best designed control systems, most of which are not presently used in the industry.

The state of the art (for existing controls) and future considerations for control technologies are discussed below.

STATE OF THE ART

Carbon Black Applications

The carbon black operation is used in SBR production to impart various desirable characteristics to the rubber. At the present time, scrubbers using water as the scrubbing liquid have been used for control of particulate emissions from this operation. A control efficiency of 95% has been reported for the scrubber itself (16). With an estimated contaminated air collection efficiency of 75%, the overall control efficiency for this source is about 70%.

TABLE 44. BEST CONTROL TECHNIQUES AND THEIR CONTROL EFFICIENCIES FOR ELASTOMERS INDUSTRY (4)[a]

Emission source	Hydrocarbons		Particulates	
	Best control	Efficiency,[b] %	Best control	Efficiency,[b] %
Styrene storage (breathing)	Floating roof	80		
Hexane storage (breathing)	Floating roof	80		
Storage area (fugitive)	Housekeeping	50 to 80		
Reactor area (fugitive)	Housekeeping	50 to 80		
Butadiene absorption	Incineration	90		
Monomer recovery area (fugitive)	Housekeeping	50 to 80		
Desolvent area (surge vent)	Improved steam stripping	50		
Desolvent area (fugitive)	Housekeeping	50 to 80		
Carbon black application			High energy scrubber	75
Size reduction			Cyclone	80
Depolymerization	Condenser and scrubber	90		
Drying	Incineration	90	—[c]	—[c]
Baling			Cyclone	70

[a] Blanks indicate no emissions from operations.

[b] The control efficiency given here is the product of the gas collection efficiency and the pollutant removal efficiency.

[c] No control is needed due to very low emission factors and source severity.

TABLE 45. BEST CONTROL TECHNIQUES AND THEIR CONTROL EFFICIENCIES FOR RUBBER PRODUCTS INDUSTRY[a]

Emission source	Hydrocarbons		Particulates	
	Best control	Efficiency,[b] %	Best control	Efficiency,[b] %
Compounding	Incineration	90	Fabric filtration	90
Milling	Incineration	60		
Calendering	Incineration	55		
Fabric cementing	Incineration	85		
Extrusion	Process change (vented extruder)	80		
Under tread cementing	Carbon adsorption	90		
Green tire Spraying	Water-base spraying	90		
Buffing			Cyclone and fabric filtration	90
Rubber cementing	Incineration	36		
Latex dipping and drying	Process change (water-based latex)	90		
Bonding of extruded parts	—[c]	—[c]		
Adhesive spraying	Incineration	70		
Molding	Incineration	60	—[c]	—[c]
Curing	Incineration	60	—[c]	—[c]
Finish painting	Process change (detergent wash)	90		

[a] Blanks indicate no emissions from operations.

[b] The control efficiency given here is the product of the gas collection efficiency and the pollutant removal efficiency.

[c] Due to difficulty in control, no control technique is identified.

Because of the small particle size of the carbon black used in the rubber industry (around 0.2 μm) (16), high-energy type scrubbers such as venturi and flooded disc types are required for high control efficiencies.

Baling Operations

Talc dusting is performed in baling operations in SBR production and rubber reclaiming to prevent the rubber product from sticking to the inside of the bag. Cyclones have been used to minimize talc losses and to control particulate emissions. Because of the large particle sizes of talc (1 μm to 20 μm), standard low resistance cyclones could be expected to achieve an overall control efficiency of 70% (16).

Desolvent Area

In the desolvent area in crumb SBR production by solution polymerization, unrecovered or unstripped butadiene, styrene, and hexane are emitted. The control option deemed most applicable is improving the efficiency of the steam stripping step of the process. The increased stripping efficiency obtained by increasing the steam-to-hexane ratio results in a 50% decrease in subsequent emissions of hydrocarbons from this source (4).

Depolymerization

In the depolymerization operation of rubber reclaiming, oily mists, solvent vapors, and other organic vapors are emitted. The emissions are vented to the atmosphere by a stack and are considered as essentially 100% collectable. Water scrubbing has been used for control of this source and can achieve 90% control efficiency for hydrocarbons (4). This control results, however, in the generation of wastewater to be treated.

Compounding

In general, emissions from Banbury mixers and rubber mills are in a finely divided form and smaller than 15 μm. Inertial separators are not, therefore, effective control devices for this service. The most common control device employed is the baghouse; a well-designed baghouse can be operated with 98% to 99.5% efficiency (17). Standard cotton sateen bags are adequate at a filtering velocity of 0.9 m/min. In some cases, scrubbers have also proved satisfactory and advantageous in scrubbing out some oil vapors and oil mists that may be present in some blends with the contaminated gas collection efficiency considered, the overall state-of-the-art control efficiency for this source was estimated at 90%.

Fabric Cementing

In the fabric cementing operation, the fabric is oven dried to drive off the carrier solvent. In a small-diameter, braided-hose plant, thermal incineration is used to reduce by 95% the hydrocarbon vapors resulting from hose-cementing operations (4). The incinerator operates at 760°C and has heat recovery to the oven itself. In another plant, solvent vapors from a fabric cementer drying oven are vented to a catalytic incinerator. The incinerator operates at about 260°C and is approximately 90% efficient (4).

In addition, carbon adsorption has been reported for at least one fabric cementer in the rubber industry. Reduction was reported to be 85%, with losses mainly attributable to solvent handling and less than 100% collection efficiency (4).

Undertread Cementing

This operation is a tackifying step used in tire manufacture where the tread is dipped in rubber cement. It is one of the few emission points where hydrocarbon control equipment is presently installed. In one plant, the total control system consists of a ventilation enclosure, which is designed to capture evaporated solvent from the cementing tank and the coated tread, and a dual-unit carbon adsorber (4).

The system has been tested and observed to have an overall control efficiency of about 94%. The design features of the ventilation system include 1) adequate dilution of the volatile vapors, 2) sufficient residence time of tread on the enclosed conveyor to ensure the capture of solvent during drying, and 3) operator accessibility to areas within the hood, especially during tread die changes (startup) and periods of scheduled maintenance. The total ventilation flow is ducted to the dual adsorber before being vented to the atmosphere. The carbon unit itself consists of two carbon beds operated on an alternating cycle of adsorbing and steam stripping. Ninety-five percent of the collected solvent is recovered by the steam stripping, condensation, and decantation steps. The recovered solvent is reused within the plant both in undertread and other cementing operations (4).

The above control system represents the best control with redesign of the existing enclosure and ventilation system. For existing plants, the vapor collection efficiency ranges from 65% to 73%, with an overall control efficiency of about 65% (18).

Green Tire Spraying

In the green tire operation, green tires are removed from a storage rack and placed in the spray booth where the spraying function is automatically accomplished. Retention time in the booth is less than 5 s. The tire is then removed and placed on another rack. Subsequent evaporation is to general room exhaust. Thus, vapor collection in the booth itself is only 44% (18). The overall efficiency for hydrocarbon emission control from this source is thus estimated to be about 40%.

FUTURE CONSIDERATIONS

A new development in the green tire spraying operation is substituting the solvent-based sprays with water-based sprays. If this is widely practiced, hydrocarbon emissions from this operation could be reduced by 90%. The inside spray, primarily needed as a release agent during curing, is currently known to be water based in several plants. The outside spray is also needed as a release agent; in addition, it helps produce an aesthetically pleasing finished product.

Development and wide use of a water-based material for the outside spray which can achieve the same effect is the key to total elimination of hydrocarbon emissions from this operation. At present, controls for hydrocarbon emissions from adhesive spraying rubber cementing, and curing (including molding) operations have not been reported. Owing to the quantities of hydrocarbons emitted and possible tighter government regulations, industries will soon have to cope with these emissions.

Adhesive spraying is used to apply adhesive to metal surfaces for metal-bonded rubber items. Control of this hydrocarbon source presents less of a problem because most of the spraying is performed in a spraying booth, and exhaust from it can be vented to a control device. However, because of the presence of solids in the excess spray aerosol, carbon bed or catalytic incinerators cannot be used unless a solid collection device is used before ether of the control devices. This is because the solid content of the spray aerosol will generate a coating on the surface of activated carbon and catalyst, and regeneration for removal of this coating will be almost impossible.

Rubber cementing is typically used in tackifying a rubber inner sole before it is placed on the outer sole, a sheet of rubber stock before wrapping it into a belt, and a rubber hose before another layer of rubber is applied. This operation is generally performed manually, and cement is used widely throughout a plant manufacturing area. The application may be by a knife, a brush, a roller, or even by hand. Control of this source is not feasible unless there is a major process change to eliminate the manual operations and to locate all such operations in a confined area. To complicate the matter, most plants have had to increase the ventilation in work areas to meet OSHA[a] requirements. The resultant large volume of air will make the control even more difficult both technically and economically.

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[a] Occupational Safety and Health Administration.

In the tire curing and general molding operations, presses are located over a large open area which is ventilated or exhausted by large plant fans. Emissions from these operations contain vaporized hydrocarbons and condensed oil mists and solid organic particles. To collect the contaminated air for treatment, a hood for each press is needed to minimize the amount of air flow. In addition, because of the presence of oil mists and organic particles, only two alternatives are feasible for treatment of the gas - thermal incineration and wet scrubbing. Wet scrubbing will generate wastewater which is difficult to treat.

The drying operation in the solution polymerization process for production of SBR is the most significant hydrocarbon emission point in terms of emission factor and source severity. There is now no control of this source in the industry (4). Since most of the hydrocarbon emission is in the form of hexane solvent (4), carbon adsorption appears to be the most feasible control technique because it recovers the solvent. However, this is complicated by the presence of the small amount of extender oil which is added to the cement before coagulation for producing "extended" SBR products. The vaporized extender oil (in the dryer) will foul the carbon bed unless condensation and mist elimination are performed before the contaminated gas enters the carbon bed. Otherwise, incineration will be the next choice for controlling this source.

SECTION 6

GROWTH AND NATURE OF THE INDUSTRY

PRESENT TECHNOLOGY

SBR Production

At present emulsion polymerization is used to produce 90% of the SBR made in the U.S. The remaining 10% of SBR is produced by solution polymerization (7). Emulsion SBR is categorized into different types; the specifications for these are related to features such as polymerization method, chemical structure, proportion of bound styrene, masterbatch type and so on, all of which information is codified using a system operated by the International Institute of Synthetic Rubber Producers (33).

In the early days of production of SBR, especially during World War II, the catalysts used were certain organic persulfates. These catalysts generated free radicals which initiate polymerization when heated to temperatures around 60°C. The SBR so obtained - "hot" SBR - contained a proportion of highly branched polymer molecules and its quality was deficient in some respects. A critical postwar development was activated catalysts, which bring about polymerization at much lower temperatures, around 5°C. SBR obtained in this way - "cold" SBR - has far fewer branched molecules and is distinctly superior to hot SBR which it has largely replaced (33).

Emulsion polymerization has a number of obvious advantages over solution polymerization. These advantages include lower viscosity, better heat transfer for removal of reaction heat, no need for recovering expensive solvent, no problems with possibly toxic solvents, easy recovery of unreacted monomer, and direct production of synthetic latexes.

Despite its apparent engineering disadvantages and complexities, solution polymerization has realized a steady build-up of capacity because of better properties possessed by solution polymerized SBR (33). It combines the best features of emulsion-polymerized SBR and polybutadiene in one rubber. There are several commercial types of solution SBR, most of which have a random arrangement of the styrene and butadiene elements along each polymer chain (31).

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(33) Blow, C. M. Rubber Technology and Manufacture. CRC Press, Cleveland, Ohio 1971.

Rubber Products Fabrication

The five basic steps involved in rubber product fabrication are: compounding, mixing, forming, building, and vulcanization.

Compounding is the process of determining the proper ingredients and proportions to be used in the rubber recipe in order to obtain the required properties of the end product. The main objectives of the mixing operation are to obtain a uniform blend of the ingredients and to achieve consistent properties from batch to batch. Mixing is presently carried out as a batch process using either a two-roll mixer or an internal (Banbury) mixer. Batch size varies according to mixing equipment capacity, which is typically from 68 kg to 136 kg for a 2.13 m mill and 454 kg or more for the largest internal mixers.

Forming operations usually consist of calendering or extrusion. Calendering involves forming the rubber compound into thin sheets, coating it on a fabric, or wiping it into a fabric by means of a series of rollers. Thin sheets of rubber are built up to make the final thickness desired, e.g., 8 to 10 sheets may be used to make a final sheet 1.6 mm thick. Extrusion is accomplished by a power driven screw in a stationary cylinder which forces the heated rubber compound through a die to give the desired shape. Other forming operations used in rubber processing include casting, blow molding, and injection molding.

Building operations vary widely according to the product being manufactured. For example, in tire manufacture, the calendered cord plies are applied to the assembly drum one at a time to build up a two-, four-, six-, or eight-ply tire.

Vulcanization, which imparts elastic characteristics to rubber, can be carried out using molds heated to 138°C for 10 min to 90 min as in tire manufacturing. Alternatively, rubber products may be cured in an autoclave with steam or water depending on the required temperature and pressure. Heated air, either at atmospheric or elevated pressure, can also be used to vulcanize products that are adversely affected by moisture. Various combinations of these cures are also used in order to achieve the desired properties in the product.

EMERGING TECHNOLOGY

SBR Production

As has been mentioned in the previous subsection, solution-polymerized SBR has several properties superior to those of emulsion-polymerized SBR. According to one reference (33), solution-polymerized SBR will overtake emulsion SBR as the work horse rubber in terms of consumption by 1980.

Another development in SBR production is introduction of thermoplastic SBR. This elastomer is produced by block copolymerization of styrene with butadiene along the polymer chains, instead of random copolymerization by the solution polymerization process. This plastic rubber has all the properties of a normal sulfur vulcanizate at ambient working temperatures and it processes as easily as polyethylene and polypropylene at higher temperatures (33).

Rubber Products Fabrication

During the 1950's and the 1960's, the rubber industry experienced a slow rate of technological advancement. However, recent years have witnessed an accelerated pace, and many new innovations are now beginning to alter the industry. For example, many plants now employ tanks and silos for bulk storage and handling of raw materials such as fillers or reinforcers. The use of large preblending systems to provide more uniform quality of raw materials is being explored. In this vein, the Farrel Company is reportedly developing technology for blending chopped or crumb rubber to even out batch-to-batch variations (34). In addition, some large production facilities now employ fully automated, computer controlled charger-mixer systems.

An improvement in the curing process is the use of cure rate integrators that employ a special sensor to accurately monitor the temperature. These devices have reportedly reduced curing times by 8% (34). Another example of the trend toward increasing automation is its use in radial tire plants. The last 2 minutes of the 5-minute tire assembly operation are now said to be automated (34).

An important advance in blending operations, that of continuous mixing, is being actively developed. The combination of an internal mixer with some type of screw mixing will permit increased mixing capacity and reduced mixing times. At present, however, this technology is considered to be several years away (34). The increasing demand for exterior automotive components made of dent-proof rubber and the steeply rising cost of energy are expected to further accelerate the development of new manufacturing processes in the rubber industry.

The new manufacturing techniques should hasten the further development of new forms of rubber and their acceptance and use by fabricators. The new forms of rubber include powdered rubber for continuous mixing, thermoplastic types which allow the vulcanization stage to be eliminated, and liquid polymers (especially polyurethanes) for use in casting and injection molding processes. One source (9) estimates that within the next 5 years, liquid and powdered rubbers will account for 20% of the total rubber material used in fabrication of rubber products in the United States.

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(34) Survey Results on Machinery, Equipment. Rubber World, 170(4):57, 1974.

MARKETING STRENGTHS AND WEAKNESSES

Tires

The future growth of the rubber industry is closely related to the automotive industry, since about two-thirds of all new rubber produced goes into automotive tires. Of this amount, about 85% on a unit basis (60% on a weight basis) goes into passenger car tires. Hence, the demand for rubber will be greatly affected by the total passenger vehicle miles driven and by tire design, which affects tread life. Average passenger car mileage for the past 10 years has increased steadily from about 15 Mm to 16 Mm annually. However, this figure is expected to remain nearly constant or even decline somewhat during the next several years due to increased fuel costs.

Tire tread life is expected to continue to increase due to the shifts to belted bias and radial tires and to small, lighter-weight cars. From 1968 to 1970, new car manufacturers switched almost completely from bias ply to belted bias tires, which offer about 25% better mileage. The switchover in the replacement tire market is proceeding at a much slower rate and is expected to stop at 35% to 40%, because the owner of an older car is less inclined to buy expensive, long-wearing tires (5).

Another factor that may adversely affect the tire market is the trend to only four tires per car. Development work toward this objective is under way at all companies (35). In addition to safety and convenience, the incentives to "eliminate the spare" include reduced car weight, more trunk space, and reduced new-car cost.

The above considerations lead to a projected increase in consumption of rubber for automotive tires from 1.95×10^6 metric tons in 1974 to 2.14×10^6 metric tons in 1980. The tire industry's percentage of total rubber consumption is expected to decrease from 68% in 1974 to 59% in 1980 (5, 35).

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(35) Rubber Products: 1974-1975. Rubber World, 171(4):27, 1975.

Molded and Extruded Products

The strengths and weaknesses of the molded and extruded rubber products markets vary with the variety of products falling in this category. In the automotive products area (especially those such as bumpers, seals, electrical wiring, etc., which are not normally replaced during the car's lifetime), the new emphasis on weight reduction of automobiles to improve gasoline mileage should result in the use of many more rubber and plastic parts.

Another area which could show substantial gains is the replacement of PVC products by rubber products. Over the past 8 years, vinyl resin products have replaced rubber in such products as wire and cable, garden hose, footwear, weather stripping, sealants, toys and auto mats. However, a trend back to rubber is developing due to rising costs of vinyl resins and the lower processing costs associated with thermoplastic elastomers (36). This trend could be accelerated because of the health problems recently associated with vinyl chloride monomer.

Rubber parts used by the oil industry in wells, platforms, refineries, and transportation of oil also have a good outlook for the immediate and long-term future due to the renewed emphasis on drilling in the United States as well as other areas of the world (37).

The Rubber Manufacturers Association's 1977 prediction for the molded, extruded, and lathe-cut sectors of the rubber business, shown in Figure 16, indicates a significant increase in dollar volume in each of the three areas (37).

The long-term strength in the molded and extruded products sector can also be inferred from the data in Reference 36 on specialty elastomers. These data suggest strong growth for all but a few specialty materials over the next 4 years. Since the use of specialty rubbers is heavy in the molded and extruded fields, the increases should be reflected in these areas.

Hose and Belting

The major strengths of the hose and belting sector of the rubber industry are in equipment for the oil and mining industries, and in automotive replacement parts.

The long-term strength of the hose and belting sector is indicated by the RMA estimates of the market potential for these products over the next 4 years as shown in Figure 17 (37).

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(36) Dworkin, D. Changing Markets and Technology for Specialty Elastomers. Rubber World, 171(5):43, 1975.

(37) Industrial Products to Grow at 7%. Rubber World, 175(4): 38-39, 1977.

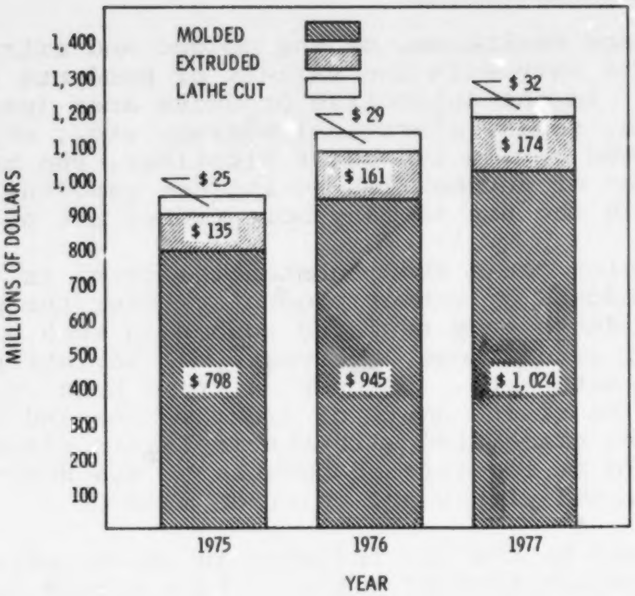

Figure 16. Domestic market estimtes and forecasts for molded, extruded, and lathe cut products (37).

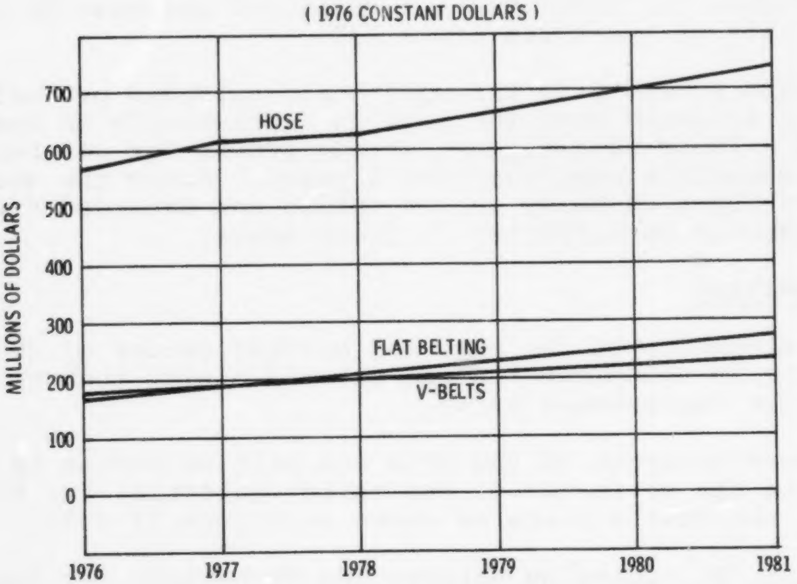

Figure 17. Market potential for rubber hose and belting (37).

New Rubber Production and Consumption

From 1960 to 1973, total new rubber consumption in the United States increased at an average annual rate of 5.4% (35). Through 1980, consumption is expected to increase at a more moderate rate, 2.4% to 3.8% (5, 39), primarily due to the effects of energy conservation programs and the socioeconomic trends in the transportation industry discussed earlier. Table 46 gives a breakdown of estimated new rubber consumption for 1980. The recent history of new rubber consumption is depicted graphically in Figure 18.

TABLE 46. RUBBER CONSUMPTION FORECAST FOR 1980 (5)
(10^6 metric tons)

Rubber type	Tires	Nontire	Total
Styrene-butadiene rubber	0.846	0.353	1.199
Polybutadiene rubber	0.324	0.036	0.360
Isoprenic rubber	0.882	0.310	1.192
EPDM rubber	0.045	0.250	0.295
Butyl or chlorobutyl rubber	0.045	0.100	0.145
Nitrile rubber	-	0.086	0.086
All other elastomers	-	0.354	0.354
TOTAL	2.142	1.489	3.631

Styrene butadiene rubber (SBR), with its major position in tire markets, currently accounts for about 60% of all synthetic rubber produced and used. Although SBR production will increase in quantity during the next few years, its percentage of total synthetic rubber is expected to decline to 57% in 1980 and 56% in 1985 (37).

Reclaimed Rubber

Most reclaimed rubber is used in automobile tires. The next area of high use is in automobile mats and automobile mechanical goods. At one time one of the prime reasons for the use of reclaimed rubber was to reduce the raw material costs of rubber compounds. This is no longer true at the present cost level of natural rubber and SBR. Although the sale of reclaimed rubber is continuing because of advantages in the area of processing (6),

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(38) Rubber Demand Faces Lower Growth Rate. Chemical and Engineering News, 52(20):12, 1974.

(39) Rubber Consumption to Increase. Rubber World, 172(2):83, 1975.

the production of reclaimed rubber has been declining in the past few years. It has been predicted (4) that this decline will continue at an annual rate of 4.5%.

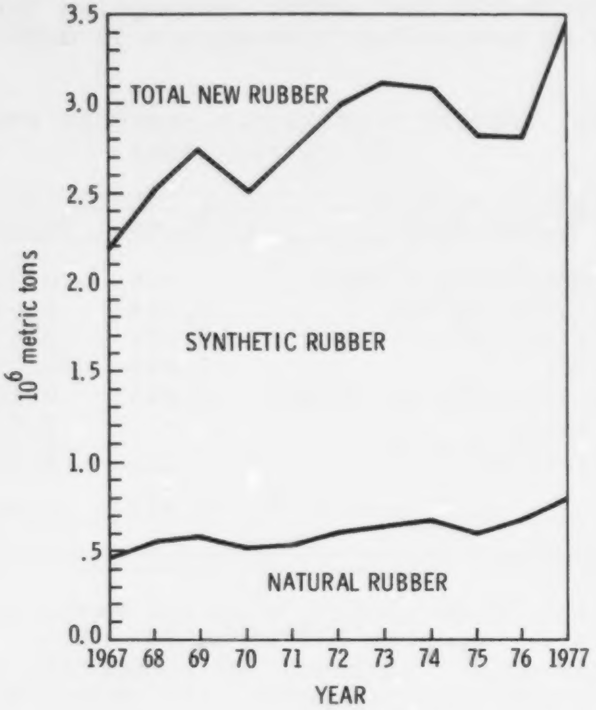

Figure 18. Total new rubber consumption, synthetic vs natural source (3).

REFERENCES

1. Standard Industrial Classification Manual, 1972. Executive Office of the President, Office of Management and Budget, Washington, D.C., 1972. 649 pp.

2. Facts and Figures for Chemical Industry. Chemical and Engineering News, 55(23):39-79, 1977.

3. Year of Recovery for Rubber Suppliers. Rubber World, 175(4):35-37, 1977.

4. Hoogheem, T. J., C. T. Chi, G. M. Rinaldi, R. J. McCormick, and T. W. Hughes. Identification and Control of Hydrocarbon Emissions from Rubber Processing Operations. Contract 68-02-1411, Task 17, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina. (Final report submitted to the EPA by Monsanto Research Corporation, July 1977.) 383 pp.

5. Richardson, J., and M. Herbert. Forecasting in the Rubber Industry. Presented at the Joint Meeting of the Chemical Marketing Research Association and the Commercial Development Association, New York, New York, May 1974.

6. Allen, P. W. Natural Rubber and the Synthetics. John Wiley & Sons, Inc., New York, New York, 1972. 255 pp.

7. Development Document for Effluent Limitation Guidelines and New Source Performance Standards for the Tire and Synthetic Segment of the Rubber Processing Point Source Category. EPA-440/1-74/013-a, U.S. Environmental Protection Agency, Washington, D.C., February 1974. pp. 31-35.

8. Morton, M. Rubber Technology, Second Edition. Van Nostrand Reinhold Company, New York, New York, 1973. 603 pp.

9. Outlook 1974 - Part II: Status Report on Elastomeric Materials. Rubber World, 169(5):38-46, 1974.

10. Shreve, N. R. Chemical Process Industries, Third Edition. McGraw-Hill Book Company, New York, New York, 1967. 905 pp.

11. Kent, J. A. Riegel's Handbook of Industrial Chemistry, Seventh Edition. Van Nostrand Reinhold Company, New York, New York, 1974. 902 pp.

12. Rosnto, D. V. Injection Molding of Rubber. Rubber World, 166(6):45-61, 1972.

13. Kirk-Othmer Encyclopedia of Chemical Technology, Second Edition, Vol. 17. John Wiley & Sons, Inc., New York, New York, 1968. 884 pp.

14. McPherson, A. T., and A. Klemin. Engineering Uses of Rubber. Reinhold Publishing Corporation, New York, New York, and Chapman & Hill, Ltd., London, United Kingdom, 1956. 490 pp.

15. 1972 Census of Manufactures, Volume II: Industry Series, Part 2: SIC Major Groups 27-34. U.S. Department of Commerce, Washington, D.C., August 1976.

16. Pervier, J. W., R. C. Barley, D. E. Field, B. M. Friedman, R. B. Morris, and W. A. Schwartz. Survey Reports on Atmospheric Emission from the Petrochemical Industry, Volume 4: Styrene Butadiene Rubber via Emulsion Polymerization. EPA-450/3-73-006d, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, June 1974. 39 pp.

17. Air Pollution Engineering Manual, Second Edition. J. A. Danielson, ed. Publication No. AP-40, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, May 1973. 987 pp.

18. Van Lierop, G., and P. W. Kalika. Measurement of Hydrocarbon Emissions and Process Ventilation Requirements at a Tire Plant. Presented at the 68th Annual Meeting of the Air Pollution Control Association, Boston, Massachusetts, June 15-20, 1975. 23 pp.

19. Rappaport, S. M. The Identification of Effluents from Rubber Vulcanization. Ph.D. Thesis, University of North Carolina, Chapel Hill, North Carolina, 1974.

20. Angert, I. G., A. I. Zenchenko, and A. S. Kuzminski. Volatilization of Phenyl-2-Naphthylamine from Rubber. Rubber Chemistry and Technology, 34(3):807, 1961.

21. Taft, W. K., M. Felton, J. Duke, R. W. Laundrie, and D. C. Prem. Oil Types in the Program for Oil Extended Rubber. Industrial and Engineering Chemistry, 47(5):1077, 1955.

22. Gaeta, L. J., et al. Antioxidant Analysis. Rubber Age, 101(6):47, 1967.

23. Marn, P. J., T. J. Hoogheem, D. A. Horn, and T. W. Hughes. Source Assessment: Solvent Evaporation - Degreasing. Contract 68-02-1874, U.S. Environmental Protection Agency, Cincinnati, Ohio. (Final document submitted to EPA by Monsanto Research Corporation, January 1977.) 180 pp.

24. Assessment of Industrial Hazardous Waste Practices--Rubber and Plastics Industry. (Prepared by Foster D. Snell, Inc., Florham Park, New Jersey, under EPA Contract 68-01-3194, for presentation to the Environmental Committee of the Rubber Manufacturers Association, Cleveland, Ohio, October 22, 1975.)

25. A Look at the Tire Industry. Rubber World, 175(4):42-46, 1977.

26. Aerometric and Emissions Reporting System (AEROS), U.S. Environmental Protection Agency. National Air Data Branch, Research Triangle Park, North Carolina 27711.

27. TLV's® Threshold Limit Values for Chemical Substances and Physical Agents in the Workroom Environment with Intended Changes for 1976. American Conference of Governmental Industrial Hygienists, Cincinnati, Ohio, 1976. 94 pp.

28. Turner, D. B. Workbook of Atmospheric Dispesion Estimates. Public Health Service Publication No. 999-AP-26, U.S. Department of Health, Education, and Welfare, Cincinnati, Ohio, May 1970. 84 pp.

29. Nonhebel, G. Recommendations on Heights for New Industrial Chimneys. Journal of the Institute of Fuel. 33:479-511, July 1960.

30. Code of Federal Regulations, Title 42 - Public Health, Chapter IV - Environmental Protection Agency, Part 410 - National Primary and Secondary Ambient Air Quality Standards, April 28, 1971. 16 pp.

31. Eimutis, E. C., and M. G. Konicek. Derivations of Continuous Functions of the Lateral and Vertical Atmospheric Dispersion Coefficients. Atmospheric Environment, 6(11): 859-863, 1972.

32. 1972 National Emissions Report. EPA-450/2-74-012, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, June 1974. 422 pp.

33. Blow, C. M. Rubber Technology and Manufacture. CRC Press, Cleveland, Ohio, 1971.

34. Survey Results on Machinery, Equipment. Rubber World, 170(4):57, 1974.

35. Rubber Products: 1974-1975. Rubber World, 171(4):27, 1975.

36. Dworkin, D. Changing Markets and Technology for Specialty Elastomers. Rubber World, 171(5):43, 1975.

37. Industrial Products to Grow at 7%. Rubber World, 175(4): 38-39, 1977.

38. Rubber Demand Faces Lower Growth Rate. Chemical and Engineering News, 52(20):12, 1974.

39. Rubber Consumption to Increase. Rubber World, 172(2):83, 1975.

APPENDIX A

DEVELOPMENT OF SOURCE SEVERITY EQUATIONS

Source severity, S, has been defined as follows for criteria pollutants:

$$S = \frac{\bar{\chi}_{max}}{AAQS} \qquad \text{(A-1)}$$

where $\bar{\chi}_{max}$ = time-averaged maximum ground level concentration
AAQS = ambient air quality standard

Values of $\bar{\chi}_{max}$ are found from the following equation:

$$\bar{\chi}_{max} = \chi_{max} \left(\frac{t_o}{t} \right)^{0.17} \qquad \text{(A-2)}$$

where t_o is the "instantaneous" (i.e., 3-min) averaging time and t is the averaging time used for the ambient air quality standard as shown in Table A-1 for particulates and hydrocarbons.

TABLE A-1. SUMMARY OF NATIONAL AMBIENT AIR QUALITY STANDARDS FOR PARTICULATES AND HYDROCARBONS (29)

Pollutant	Averaging time	Primary standards	Secondary standards
Particulate	Annual (geometric mean)	75 $\mu g/m^3$	60[a] $\mu g/m^3$
	24 hr[b]	260 $\mu g/m^3$	150 $\mu g/m^3$
Hydrocarbons (nonmethane)	3 hr (6 to 9 a.m.)	160 $\mu g/m$ (0.24 ppm)	(Same as primary)

[a] The secondary annual standard (60 $\mu g/m^3$) is a guide for assessing implementation plans to achieve the 24-hr secondary standard.

[b] Not to be exceeded more than once per year.

HYDROCARBON SEVERITY

The primary standard for hydrocarbon is reported for a 3-hr averaging time. Therefore, t = 180 min. Hence, from Equation A-2:

$$\overline{\chi}_{max} = \chi_{max} \left(\frac{3}{180}\right)^{0.17} = 0.5\chi_{max} \tag{A-3}$$

Substituting for χ_{max} from Equation 6 (Section 4) yields:

$$\overline{\chi}_{max} = \frac{(0.5)(0.052)Q}{H^2} = \frac{0.026\ Q}{H^2} \tag{A-4}$$

For hydrocarbons, the AAQS = 1.6×10^{-4} g/m^3. Therefore

$$S = \frac{\overline{\chi}_{max}}{AAQS} = \frac{0.026\ Q}{1.6 \times 10^{-4}\ H^2} \tag{A-5}$$

$$S = \frac{162.5\ Q}{H^2} \tag{A-6}$$

PARTICULATE SEVERITY

The primary standard for particulate is reported for a 24-hr averaging time. Therefore, t = 1,440 min. Hence, for Equation A-2:

$$\overline{\chi}_{max} = \chi_{max} \left(\frac{3}{1{,}440}\right)^{0.17} \tag{A-7}$$

Substituting for χ_{max} from Equation 6 (Section 4) yields:

$$\overline{\chi}_{max} = \frac{0.052\ Q}{H^2}\ (0.35) = \frac{0.0182\ Q}{H^2} \tag{A-8}$$

For particulates, AAQS = 2.6×10^{-4} g/m^3. Therefore

$$S = \frac{\overline{\chi}_{max}}{AAQS} = \frac{0.0182\ Q}{2.6 \times 10^{-4}\ H^2} \tag{A-9}$$

or

$$S = \frac{70\ Q}{H^2} \tag{A-10}$$

APPENDIX B

MASS EMISSIONS OF HYDROCARBONS AND PARTICUTATES BY STATE AND BY SIC

The state-by-state listing of emissions from rubber processing industries was obtained by distributing the national emissions (as shown in Table 40) among the states according to the number of plants in the applicable states (as shown in Table 23). Tables B-1 and B-2 show the calculated mass emissions for hydrocarbons and particulates, respectively, in each state for each of the 9 industries. These state-by-state mass emissions were used in the calculation of percent contribution of hydrocarbon and particulate emission from rubber processing to the corresponding total state emissions presented in Tables 41 and 42.

TABLE B-1. MASS EMISSIONS OF HYDROCARBONS FROM RUBBER PROCESSING BY SIC[a] (metric tons/yr)

State	SIC 2822	SIC 3031	SIC 3011	SIC 3021	SIC 3041	SIC 3069	SIC 3293	SIC 3357	SIC 7534[b]	State total
Alabama			1,600			61	20		28	1,700
Arizona			320			39			10	370
Arkansas			800	270	42	33			16	1,100
California	410		[illegible],500	1,100	290	800	190	21	250	6,500
Colorado			480		42	17	13		10	560
Connecticut	210	83	160	270	42	260	40	21	72	1,100
Delaware	210		160		120	11			8	510
Florida			320	540		120	7		32	1,000
Georgia	410		1,400	540		170		10	54	2,600
Illinois	210	42	1,600	270	210	340	150	10	120	2,900
Indiana			800	540	84	310	34	10	86	1,900
Iowa			800			28			12	840
Kansas			320						2	320
Kentucky	410		480			22	7	10	12	940
Louisiana	620								4	620
Maine			160	810					4	970
Maryland			320	540		60	13		20	950
Massachusetts	410		960	1,600	120	360	60	21	110	3,600
Michigan	210		960		84	320	80		94	1,700
Minnesota			160		42	130	27		36	400
Mississippi		42	480			61			18	600
Missouri			640	540	42	72	34		30	1,300
Nebraska						28			6	34
Nevada					84				2	86
New Hampshire			480	1,100		11	7		12	1,600
New Jersey			480	540	500	390	74	10	120	2,100
New York		42	640	1,300	170	380	94	21	120	2,800
North Carolina	410		1,100	540	42	100	20	10	40	2,200
Ohio	410	42	4,300	810	420	970	120	21	280	7,400
Oklahoma			1,100			39	20		20	1,200
Oregon			480			61			16	560
Pennsylvania	410		2,200	1,300	120	270	80	10	100	4,500
Rhode Island						89			20	110
South Carolina			320		42	50			14	430
South Dakota						6				6
Tennessee	410		2,100	810	42	72	13		40	3,500
Texas	1,200		1,800			220	110		86	3,400
Utah					42	28	13		10	93
Vermont						6				6
Virginia			800			72	7		22	900
Washington			320			28			8	360
West Virginia				270		44	13		12	340
Wisconsin			320	270		130	34		38	790
Nationwide	6,000	250	33,000	14,000	2,600	6,200	1,300	180	2,000	65,500

[a] Blanks indicate no emissions from the industry.

[b] There is a lack of data available for geographical distribution of tire retreading shops. In this calculation, the percentage distribution of plants among state was assumed to be the same as that given in Table 23 for the total of the other eight industries.

TABLE B-2. MASS EMISSIONS OF PARTICULATES FROM RUBBER PROCESSING BY SIC[a]
(metric tons/yr)

State	SIC 2822	SIC 3031	SIC 3011	SIC 3021	SIC 3041	SIC 3069	SIC 3293	SIC 3357	SIC 7534[b]	State total
Alabama			350			30	8		13	400
Arizona			71			19			5	95
Arkansas			180	8	7	17			8	220
California	28		780	31	50	400	75	6	120	1,500
Colorado			110		7	8	5		5	140
Connecticut	14	30	35	8	7	130	15	6	34	280
Delaware	14		35		21	6			4	80
Florida			71	16		61	2		15	160
Georgia	28		320	16		86		3	26	480
Illinois	14	15	350	8	35	170	57	3	57	710
Indiana			180	16	14	160	13	3	41	430
Iowa			180			14			6	220
Kansas			71						1	72
Kentucky	28		110			11	2	3	6	160
Louisiana	42								2	44
Maine			35	23					2	60
Maryland			71	16		28	5		10	130
Massachusetts	28		210	46	21	180	23	6	52	570
Michigan	14		210		14	160	31		45	470
Minnesota			35		7	67	10		17	140
Mississippi		15	110			30			8	160
Missouri			140	16	7	36	13		14	230
Nebraska						14			3	17
Nevada					14				1	15
New Hampshire			110	31		5	2		6	150
New Jersey			110	16	85	190	28	3	56	490
New York		15	140	38	28	190	44	6	57	520
North Carolina	28		250	16	7	50	8	3	19	380
Ohio	28	15	960	23	70	480	46	6	130	1,800
Oklahoma			250			19	8		10	290
Oregon			110			30			8	150
Pennsylvania	28		500	38	21	140	31	3	49	810
Rhode Island						44			10	54
South Carolina			71		7	25			7	110
South Dakota						3				3
Tennessee	28		460	23	7	36	5		19	580
Texas	85		390			110	41		41	670
Utah					7	14	5		5	31
Vermont						3				3
Virginia			180			36	2		10	230
Washington			71			14			4	90
West Virginia				8		22	5		6	41
Wisconsin			71	8		67	13		18	180
Nationwide	410	91	7,300	400	440	3,100	500	56	950	13,200

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[a] Blanks indicate no emissions from the industry.

[b] There is a lack of data available for geographical distribution of tire retreading shops. In this calculation, the percentage distribution of plants among state was assumed to be the same as that given in Table 23 for the total of the other eight industries.

GLOSSARY

accelerator: Compound which reduces the time required to vulcanize (cure) synthetic or natural rubber.

activator: Metallic oxide that makes possible the crosslinking of sulfur in rubber vulcanization (curing).

adhesive spraying: Operation by which adhesive material is sprayed onto the metal surface for subsequent fabrication of metal-bonded rubber goods.

affected population: Number of people around a representative plant who are exposed to high concentrations of pollutants.

antioxidant: Organic compound added to rubber to retard oxidation or deterioration.

atmospheric stability class: Class used to designate degree of turbulent mixing in the atmosphere.

banbury mixer: Trade name for a common type of internal mixer manufactured by Farrel Corporation; used in compounding and mixing of rubber stock.

calendering: Operation by which rubber stock is pressed between rolls to make smooth or to thin into sheets.

camel back: Tire tread used in the retreading of tire carcasses.

cementing: Application of a material consisting of polymeric rubber solids dissolved in solvent to rubber surface or fabric for good adhesion.

coagulation: Combination or aggregation of previously emulsified particles into a clot or mass.

criteria pollutants: Particulates, sulfur dioxide, hydrocarbons, carbon monoxide, and nitrogen oxides, for which national ambient air quality standards have been established.

crumb: Small coagulated particles of synthetic rubber.

curing agents: Substances which bring about the rubber cross-linking in curing process.

devulcanization (depolymerization): Softening of cured rubber by heat and chemical additives during reclaiming.

emission factor: Weight of material emitted to the atmosphere per unit weight of product or raw material consumed.

emulsion: Stable mixture of two or more immiscible liquids held in suspension by small percentage of substances called emulsifiers.

extender: Low specific gravity substance used in rubber formulations chiefly to reduce unit product costs.

extrude: Shape by forcing a material through a die.

filler: High specific gravity compound used in rubber mixture to provide a certain degree of stiffness and hardness and to decrease costs.

flash: Overflow of cured rubber from a mold.

fugitive emissions: Gaseous and particulate emissions that result from industrial related operations, but which are not emitted through a primary exhaust system, such as a stack, flue, or control system.

hazard factor: Value equal to the primary ambient air quality standard for criteria pollutants or to a reduced TLV for noncriteria pollutants.

latex: Suspension of rubber particles in a water solution.

monomer: Compound of a relatively low molecular weight which is capable of conversion into polymers.

noncriteria pollutant: Emission species for which no ambient air quality standard has been established.

pigment: Any substance that imparts color to the rubber.

plastic: Capable of being shaped or molded with or without the application of heat.

reclaimed rubber: Depolymerized (devulcanized) scrap rubber, either natural or synthetic.

reinforcing agents: Fine powders, such as carbon black, zinc oxide, and hydrated silicas, which are used to increase the strength, hardness, and abrasion resistance of rubber.

SBR: Styrene butadiene rubber, a synthetic rubber made by either emulsion or solution polymerization of styrene and butadiene.

soapstone: Substance used to prevent rubber stocks from sticking together during periods of storage.

source severity: Ratio of time-averaged maximum ground level concentration of each emission species to its corresponding ambient air quality standard (for criteria pollutants) or to a reduced TLV (for noncriteria emissions).

tire bead: Coated wires inserted in the pneumatic tire at the point where the tire meets the steel rim on which it is mounted.

tire cord: Woven synthetic or natural fabrics impregnated with rubber which form the body of the tire and supply it with most of its strength.

tire tread: Riding surface of the tire.

vulcanization (curing): Process by which plastic rubber is converted into the elastic rubber or hard rubber state.